Wally's   Carbon World

Wally Broecker

ELDIGIO Press 2014

Revised 2015

Table of Contents

Foreword

I have spent my entire 60-year career researching aspects of the Earth's carbon cycle. Although best known for my papers and books concerned with glacial cycles, ocean chemistry and global warming, I have a long-standing interest in reconstructing the longer term changes in Earth chemistry. I was among the first to challenge the idea that the ocean's chemistry composition was set by thermodynamic equilibria. In a paper published in *Quaternary Research* in 1971, I presented a kinetic model. Rather than being at thermodynamic equilibrium, the concentration of each constituent was set by the requirement that its rate of removal to sediments match the rate of addition from rivers and volcanoes. Any imbalance between input and loss would be eliminated by a feedback loop. This concept gave the ocean far more latitude for composition changes. Rather than being slave to temperature, its composition could be influenced by a wide range of tectonic and environmental changes. Buffeted about by changes both on the supply side and on the removal side, the CO_2 content of the atmosphere has undergone large changes. These changes have served as the primary driver of Earth climate.

Although I've been only a minor player in the development of thinking in this area, through my class on the Earth's carbon cycle, I have long pondered this subject. Now 43 years after I proposed a kinetic model for ocean chemistry, I have decided to put my thoughts on paper. Rather than a treatise, what I have written is aimed at challenging further thought and debate regarding how the Earth's carbon cycle works. Much of this involves my way of viewing things. As we have a long way to go before any of it can be set in concrete, much of what I say will likely turn out to be wrong. But in the interim, I hope it will provide grist for thought and discussion.

You will note that the length of the chapters varies widely. This reflects my familiarity with the subject matter. In those cases where I have a strong familiarity, they are long and in those where I am far from expert, they are quite short.

Chapter 1

Overview

The greenhouse gas carbon dioxide has had the starring role in the story of Earth's climate. It came on stage when our planet was a youngster. At its birth, 4.5 billion years ago, the Sun's energy output was only three quarters of what it is now. We know this because the evolution of the Sun's energy output is related to the number of nuclear entities present in its interior. The conversion of four hydrogen nuclei to one helium nucleus slowly reduces this number (Fig. 1-1). This reduction alters the balance between the sun's thermally-driven tendency to expand and its gravity-driven tendency to contract. As a consequence, the Sun's size has steadily decreased. As it does so, gravitational energy is released heating up its interior and thereby accelerating the rate of fusion of hydrogen nuclei. The extra heat produced in this way balances the tendency to contract. Hence, a balance is maintained. The rate of conversion of hydrogen to helium in today's Sun can be calculated from its energy output. Consequently it is possible to back calculate the evolution of its energy output. The answer comes out that over the last 4.5 billion years it has increased by about 25 percent.

If during the Earth's childhood, its atmosphere were to have had a composition similar to today's, there would have been no liquid water on its surface. Rather, it would have been frozen. Yet, as far back as our geologic record extends, there is evidence for the presence of liquid water. So clearly, early on our atmosphere must have contained more greenhouse gas than today. Any molecule made up of three or more atoms has the capability of capturing quanta of infrared radiation given off by the Earth's surface. Water (H_2O), carbon dioxide (CO_2), and methane (CH_4) qualify but oxygen (O_2), nitrogen (N_2) and argon (Ar) do not. When a greenhouse molecule captures a quantum of Earth 'light', it jumps into an unstable energy state. It then promptly returns to its ground state by emitting an identical quantum of infrared radiation. But, as the direction of this emission is random, only half of these quanta head outward (Fig. 1-2). The other half head back toward the Earth's surface. So if, for some reason, the amount of energy carried by the infrared light leaving the Earth were to fall short of matching the energy

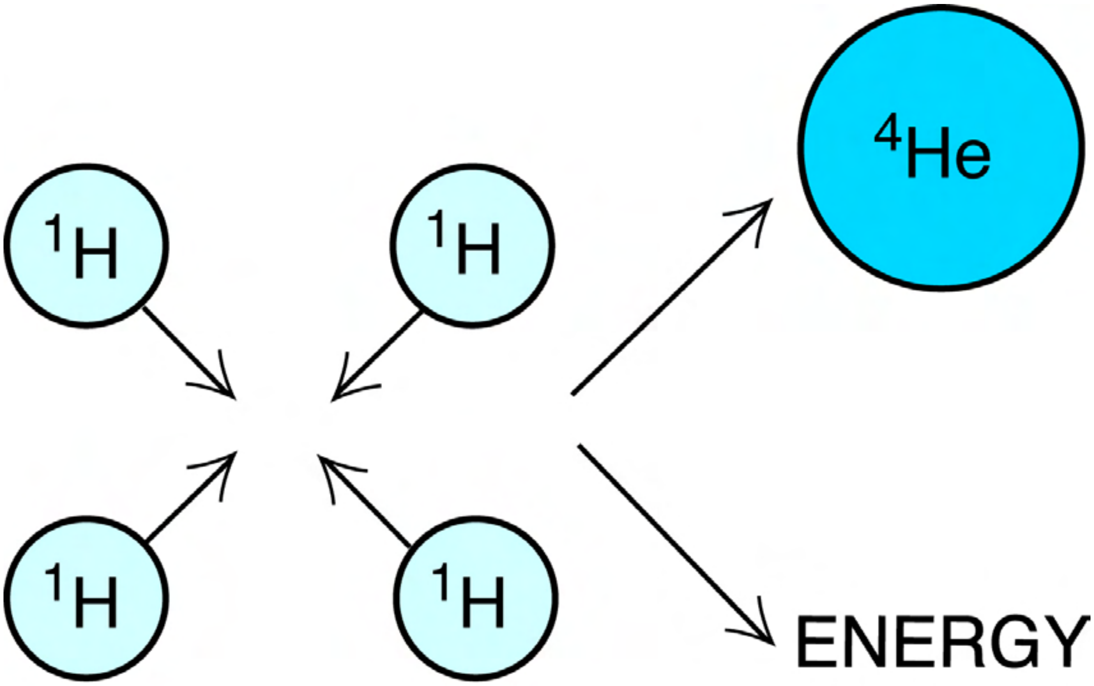


Figure 1-1. The energy released as a result of mergers of four hydrogen nuclei to form a single helium nucleus keeps the interior of our Sun hot. These mergers also decrease the number of entities whose thermal motion prevents the Sun's collapse. In order to compensate for this decrease, the Sun has burned ever brighter.

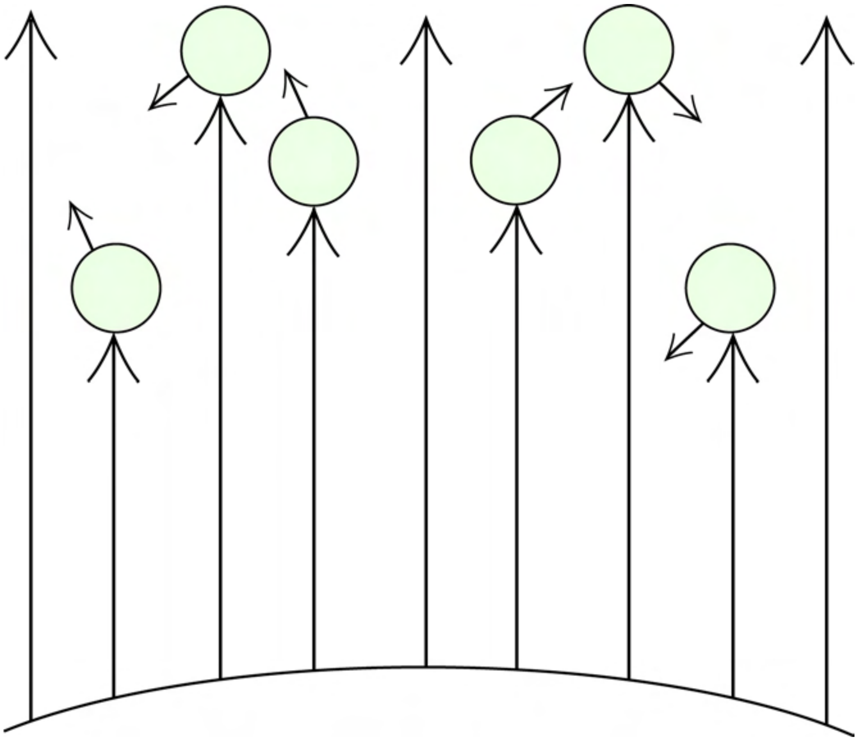


Figure 1-2. Greenhouse gases have the capability to capture quanta to infrared light given off by the Earth's surface. They promptly release the extra energy captured in this way by emitting a quantum of infrared light. But, as the direction of these emissions is random, half head back to the Earth's surface. Were an imbalance between incoming sunlight and outgoing Earth light to develop, the planet would either heat up or cool off. This would make a corresponding change in the number of quanta given off by the Earth's surface. The heating or cooling would continue until the balance between energy loss and energy gain was restored.

delivered by input of sunlight, the Earth's surface would heat up and give off additional infrared quanta. This heating would continue until the energy loss once again matched the energy gain from the Sun. This is what is happening today as we add CO_2 to the atmosphere by burning of fossil fuels.

Clearly then, if the early Sun was weaker and if the early Earth's temperature was above freezing, there must have been more greenhouse gas in the atmosphere. Currently water molecules in our atmosphere have by far the greatest greenhouse impact. But, as their amount is set by the surface ocean's temperature, they could not have prevented a freeze over. This leaves CO_2 as the most likely candidate. But, other so-called 'reduced' gases, such as CH_4 and H_2S may have also been present in sizable quantities in the young Earth's oxygen-free atmosphere. Likely so, but regardless, CO_2 must have been the primary warming agent.

If the greenhouse gases which kept the young Earth from freezing had remained in the atmosphere, as the Sun's luminosity increased, the Earth would have become very hot. So hot that its water would have been transformed to steam. As there is no evidence that this happened, these early Earth saviors must have been removed from the atmosphere. As we shall see, throughout Earth history, the CO_2 content of our atmosphere has gone up and down. Today, only a tiny fraction of the Earth's carbon is in the form of CO_2 gas.

The planet Venus reminds us that not all planets evolved in the same way as the Earth. Venus has an atmosphere 100 times more dense as ours. Further, it consists of nearly pure CO_2. The amount of carbon present as CO_2 in the Venusian atmosphere is about the same as the amount of carbon locked up in limestone on Earth. This immense load of greenhouse gas makes the surface of Venus so hot that any limestone would be dissociated into CaO and CO_2. We are not sure why Venus, a planet which in most ways is the Earth's twin, suffered a runaway greenhouse heating. Perhaps its quite different evolution is related to its slow spin. Were its atmosphere initially like ours, its 254 times longer day would lead to an incredibly large night to day temperature swings. Perhaps, as a consequence, life could not take hold on Venus.

Although our Earth escaped freeze-ups during its childhood, it was not so lucky later in life. Something went wrong 730 million years ago and the Earth became a snowball. The likely cause of this freeze up was a deficiency of CO_2 in our atmosphere. Fortunately, (at least by Earth standards) this freeze-up was short lived. We were rescued by CO_2. Even though its surface was frozen solid, the Earth's interior continued to churn. This churning was propelled by the heat produced by the decay of the long-lived radioisotopes of potassium, uranium and thorium. This churning drives the subduction of its crust into the Earth's hot interior. Any $CaCO_3$ contained in the subducted slabs is dissociated into CO_2 and CaO. The CO_2 gradually leaks back to the surface. During snowball episodes there were no rivers to supply Ca++, nor an ocean in which to precipitate $CaCO_3$. This being the case, the CO_2 released from its interior accumulated in the atmosphere strengthening its greenhouse power. The greenhouse heating continued until after several million years it more than compensated for the sunlight reflected from the Earth's icy surface. Melting began. As sunlight absorbing ocean and land replaced sunlight reflecting ice, the Earth was transformed from an icehouse to a hothouse. This elevated temperature was a result of atmosphere's huge CO_2 content coupled with the large reduction in its reflectivity.

With the ocean unfrozen, $CaCO_3$ could once again precipitate. Rains made acid by the atmospheres high CO_2 content attacked earth rocks delivering large amounts of CaO to the ocean. This CaO combined with the excess CO_2 to produce $CaCO_3$. In this way the atmosphere's CO_2 content was gradually drawn down, returning the Earth to its pre-snowball state where it remained for some 50 million years. But, whatever caused the first snowball episode struck again 650 million years ago producing a second snowball. Once again, the Earth was rescued from its frozen state by the buildup of CO_2. This sequence was repeated for a third time about 540 million years ago. It has not happened again.

The warming which followed the third of the snowball episodes ushered in an entirely new cast of creatures. The single-celled organisms, which up until that point had been the dominant life form, were eclipsed by a wide range of multi-celled organisms. Best known among these was the trilobite (Fig. 1-3), an organism with all the basic features common to today's animals. Not only did it usher in a whole set of new organisms but also the reasonably stable climate which has persisted for the last 540 million years.

How do we know that the Earth was a snowball? The evidence comes from sediments whose makeup matches that of those produced by today's glaciers, namely a heterogeneous mixture of coarse rock fragments, silts and fine clays. Further, based on the direction of their built-in magnetic vectors, some of these so-called diamictons must have formed in the tropics. As snowlines in today's tropics are 5000 meters above the ocean, to have tropical glaciers at sea level required a profound cooling. Additional evidence comes from sediments formed in the immediate aftermath of the freeze-up. Consistent with the CO_2 bailout are the so-called cap carbonates which directly overlie the glacial deposits. They represent the $CaCO_3$ precipitated during the hothouse episodes. Some of these differ from ordinary limestones in that they have large blade-like crystals, probably the result of their rapid growth.

Although these frozen Earth episodes should perhaps have squelched life altogether, instead they allowed it to take a huge step forward. Somehow the niches vacated by the extinctions caused by the freeze-up were re-occupied by a new cast of more sophisticated organisms. It makes one wonder what would have transpired if these freeze-ups had not occurred.

Even though there have been no more snowball incidents during the course of the last 540 million years, life on earth experienced two major catastrophes. One occurred 250 million years ago, killing off all but 10 to 20 percent of the species then extant. A second catastrophe occurred 70 million years ago killing off 50 or so percent of the species then extant. At the time of both extinction events massive flood basalts erupted. One hypothesis is that the extinctions were caused by volcanic emissions. If so, perhaps CO_2 was involved.

There is however a major difference between the two extinction events. Although that at 70 million was accompanied by the impact of a large asteroid, there is no evidence that a collision accompanied that at 250 million years ago. Hence it is not clear whether it was the collision or the basalt eruption that caused the extinction of half of the world's species 70 million

Figure 1-3. Trilobites appeared one-half billion years ago at the onset of the Cambrian. They serve as the flagship for the fleet of the advanced life forms absent during the first 90 percent of Earth history. Their present-day ancestor is the horseshoe crab.

years ago. Since the onset of the Cambrian (540 million years ago), the Earth's climate system with few exceptions has been well behaved. And with a few exceptions, has steered a steady course. But in order to keep climate on track, both the greenhouse power of the atmosphere and the chemical composition of sea salt have undergone changes. The quest of this book is to attempt to identify these changes.

Evidence exists which demonstrates that over much of its history, the Earth was warmer than it is today. If so, it is likely that this warmth was maintained by CO_2 contents larger than now. Of particular interest is a warm event of 50 or so thousand years' duration which occurred 55 million years ago. It is known as the Paleocene-Eocene Thermal Maximum (PETM), it involved an abrupt warming of our planet. It was first noted by a blip in the records of both oxygen and carbon isotopes for a sediment core from the Southern Ocean. The ^{18}O shift corresponded to a 5°C warming and the ^{13}C shift to the addition of more than 1000 billion tons of ^{13}C-depleted CO_2. Although widely attributed to methane released from continental margin clathrate deposits, recent studies of coastal sediments suggests that the CO_2 addition occurred in less than two decades. The evidence for the rapid delivery of the CO_2 comes from what appears to be annually-layered sediments deposited 55 million years ago on the then coastal plain extending from what is now New Jersey to what is now Virginia. The carbon isotope shift commences at the base of this layered unit. The full decline occurs in 13 layers (presumably 13 years). If indeed the decline was this rapid, it could only be caused by the impact of an extra-terrestrial object. Only a comet (Fig. 1-4) could deliver such a mass of CO_2 on such a short time scale. As comets contain about 10 percent CO_2, the diameter of the impactor delivering 1000 billion tons of CO_2 would have to have been a whopping 14 km! As the impact of a mass this large traveling at the speed of a comet would have been colossal, a host of extinctions would be expected. Yet, none of significance occurred. So we have a dilemma!

This event is of particular interest since we are poised to burn in a hundred or so years a substantial portion of the 3000 gigatons of carbon locked up in our fossil fuel reserves. The 5°C warming generated by the PETM CO_2 offers an analogue for the warming to be generated by our

Figure 1-4. A myriad of comets whirl around in the so-called Kuiper belt which lies beyond the orbit of Pluto. They contain large amounts of carbon monoxide and carbon dioxide. Now and then a comet with a highly elliptical orbit comes close enough to be seen with the naked eye. I would like to believe that 55 million years ago a sizable one crashed into the Earth triggering the PETM.

ongoing dependence on coal, oil and natural gas. As shown by modeling aimed at explaining the duration of the carbon isotope anomaly, U. of Hawaii's Richard Zeebe makes a case that the initial abrupt increase in CO_2 must have been followed by a secondary increase spread over tens of thousands of years. This additional CO_2 may well have been produced by the oxidation of methane released from continental margin clathrates. Are we about to induce such a release?

The oxygen isotope record kept in the shells of benthic foraminifera tells us that 50 million years ago, the deep ocean began to cool. It appears that this cooling was a consequence of the collision between the northward drifting Indian subcontinent and Asia. Not only did this collision create the Himalayan mountain chain, but it also forced a reorganization of the Earth's plate motions. One consequence was a drawdown in the atmosphere's CO_2 content which cooled the planet. This drawdown was presumably the result of some combination of a reduction of planetary outgassing and more efficient continental weathering.

This cooling culminated in a series of glacial cycles each lasting about 100,000 years (Fig. 1-5). Each of these cycles was terminated by an abrupt warming. The onset of the last of these warmings began 18,000 years ago ushering in the Holocene, a period of interglaciation during which our civilization has evolved.

My read is that these glaciations were driven by some combination of the uptake of CO_2 by the ocean and a reduction of CO_2 outgassing from the Earth's interior. Sixty times more carbon resides in the ocean as carbon dioxide, bicarbonate and carbonate than as CO_2 in the atmosphere. Both the cycles of soft tissue and of $CaCO_3$ manufactured by surface-dwelling plankton work to transfer carbon from the surface ocean to the ocean's interior. As the CO_2 content of surface ocean water dictates that in the atmosphere, one might say that organisms in the surface ocean have driven the Earth back and forth between its glacial and its interglacial condition. Superimposed on the drop in CO_2 generated by its uptake by the ocean was a drop in the delivery of CO_2 from volcanoes. The weight of glacial ice cover on volcanoes is thought to have shut down their output of lava and its associated gases. Hence, the reduction in the input of

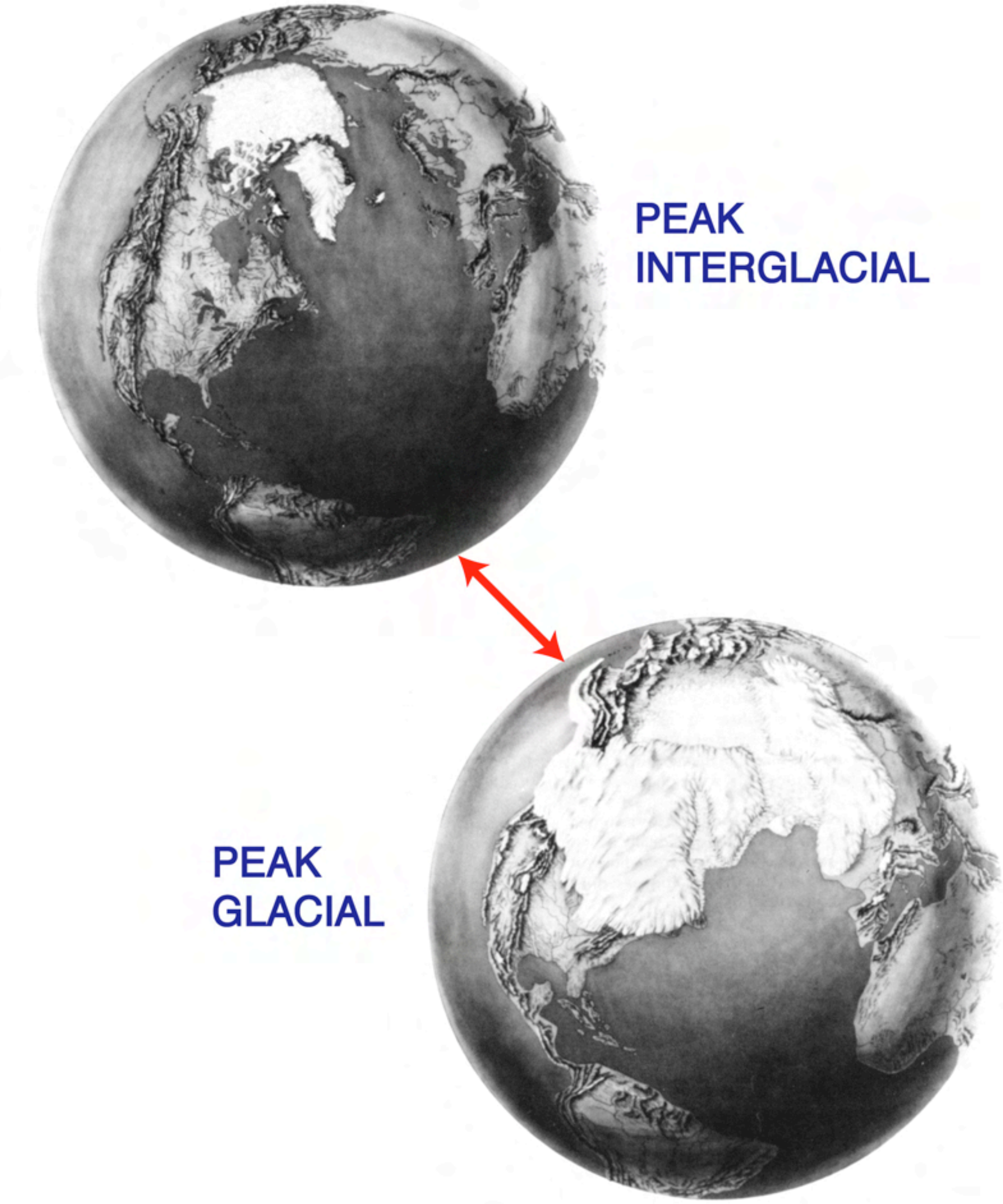


Figure 1-5. During the last half-million years, Earth climate has swung back and forth between small ice-cover and large-ice cover episodes. Each such cycle lasted about 100 thousand years. These glaciations were driven by drawdowns of the atmosphere's CO_2 content.

CO_2 from volcanoes would have enhanced the drawdown of atmospheric CO_2. This reduction of planetary CO_2 release may be responsible for the ramp-like decline which characterizes each of the Earth's 100-kyr-duration glacial cycles.

Lastly, one reason for writing this book is that we are in the midst of a man-made increase in atmospheric CO_2 content. Before the Industrial Revolution, the CO_2 content of the atmosphere was 280 parts per million. At this writing it had reached 400 ppm. Were we to burn a major portion of our fossil-fuel reserves, CO_2 would rise to above 1000 ppm. Model simulations suggest that for each doubling of the atmosphere's pre-Industrial CO_2 content, the temperature will rise by about 3°C (Fig. 1-6). Hence were we to quadruple the CO_2 content (i.e., raise it to 1120 ppm), the expectation is that the planet would warm by as much as 6°C. Despite 40 years of fretting, little progress has been made to deal with this threat.

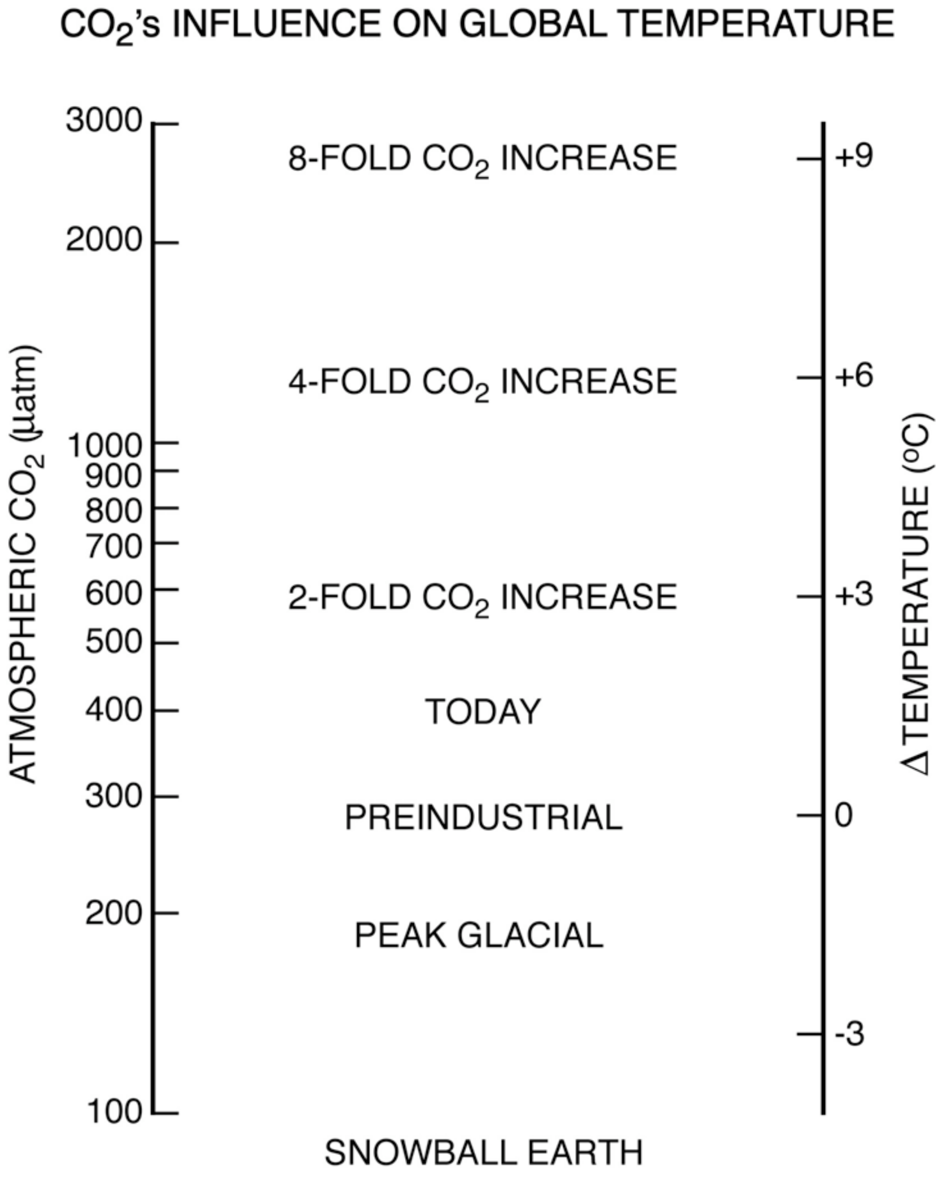


Figure 1-6. The relationship between atmospheric CO_2 content and the Earth's temperature is logarithmic. The temperature scale adapted here is based on model simulations. As these models have numerous parameters whose assigned values are uncertain, the 3°C could be anywhere in the range 1.5°C to 5.5°C. It must be kept in mind, however, that this scale is valid only for today's Earth. The many feedbacks appropriate for today's Earth were somewhat different under past conditions. Hence, the sensitivity to CO_2 changes has likely varied during the course of Earth history.

Chapter 2

Controls

Although the primary goal of this book is to understand how the atmosphere's CO_2 content has varied with time, it is necessary to consider as well what went on in the ocean. For just as the water vapor in the atmosphere is supplied from the ocean, so also is its carbon dioxide. Unlike the situation for water vapor where the temperature of the surface ocean rules, the situation for carbon dioxide is complex. In addition to surface ocean's temperature, we need to know its alkalinity and its total dissolved inorganic carbon content.

In order to understand why this is the case, we must have an understanding of alkalinity. It is defined as the difference in the ionic charge carried by the cations (Na^+, K^+, Mg^{++}, Ca^{++},…) and that carried by the anions Cl^-, $SO_4^=$,…). In today's ocean, the sum of the plus charges is slightly greater than that of the minus charges. I like to refer to this as the negative charge deficit. As seawater must be electrically neutral, additional negatively charged ions must make up the difference. In the pH range of interest (i.e., 8.0 ± 0.5), the ions listed above cannot change their charge state. This being the case, the deficit must be matched by species that can change their charge state. Two constituents of seawater serve in this capacity, i.e., carbon and boron. Carbon can be electrically neutral (as CO_2), singly charged (as HCO_3^-) or doubly charged (as $CO_3^=$). Boron can be electrically neutral (as H_3BO_3) or singly charged (as $H_4BO_4^-$). Hence, by shifting back and forth among charge states, these ions can balance a range of alkalinities (i.e., negative charge deficits). Important to us is that changes in alkalinity not only result in changes in the ratio of HCO_3^- to $CO_3^=$, but also in the CO_2 gas content of the water.

$$[CO_2] \text{ x } [CO_3^=] = K\,[HCO_3^-]^2$$

K is the chemical equilibrium constant. It depends on temperature, pressure, and ionic composition. In today's ocean bicarbonate ion is the dominant species. Hence, were the carbonate ion concentration forced to rise in order to accommodate a rise in alkalinity, the CO_2 concentration would fall by roughly the same fraction as the $CO_3^=$ went up.

As an example of the role of alkalinity consider the difference between warm surface water and deep water in today's ocean. Organisms living in the surface ocean decrease its alkalinity (i.e., negative charge excess) by removing positively charged calcium to produce $CaCO_3$ hard parts. Much of this $CaCO_3$ dissolves in the deep sea increasing its negative charge deficit. Of course, this is not the only change calcifiers make. The $CaCO_3$ removes carbonate ion from surface water and adds it to deep water. Further, soft tissue produced at the ocean's surface falls to the deep sea where it is eaten. This transfers CO_2 from surface to the deep ocean. Due to its small volume, it is the composition of surface water that is altered by the production of $CaCO_3$ and soft tissue. In particular, its CO_2 content is changed. Reconstructing the difference between the CO_2 content for the surface ocean and that for the deep ocean constitutes a large challenge in our quest to understand the carbon chemistry of past oceans and atmosphere. A knowledge of what went on downstairs does not allow us to say what went on upstairs and vice versa.

In order to get a handle on this, it is necessary to understand not only the controls on the concentrations of carbon and calcium, but also that of the element phosphorus for it is the limiting ingredient for plant growth. The bulk of the ocean's phosphate is stored in the ocean's interior. Upwelling brings it to the surface where much (but not all) of it ends up in organic tissue which sinks to the interior where it is efficiently returned to dissolved form. The unutilized PO_4 follows the movement of water through the ocean. It is also necessary to understand what controls the availability of O_2. Given adequate O_2, virtually all the organic matter reaching the deep sea is eaten. In the absence of adequate O_2, the water goes anoxic and sulfur becomes a major player.

The bottom line is that life in the ocean plays a critical role in setting the CO_2 content of surface water and hence also that of the atmosphere. Further, life's impact is limited by the availability of PO_4 and O_2.

For each of the constituents of the ocean-atmosphere reservoir, there is a feedback loop which controls its throughput. At steady state, the amount of each constituent being buried in the sediment must match that being added by volcanic emissions and by continental weathering. If, for some reason, the match between input and output is disrupted, this feedback loop will kick into operation. Through its action the mismatch is corrected. The timescale for these readjustments is closely related to the residence times of various constituents in the ocean-atmosphere reservoir. These residence times range from a few days for iron to billions of years for chloride.

Of primary interest is the situation for the element carbon. Much of what we know comes from the perturbations the carbon cycle has undergone rather than from its day to day steady-state operation. Measurements on air trapped in Antarctic ice tells us that during the last half million years, the CO_2 content of the atmosphere has swung back and forth between a glacial level of about 190 ppm and an interglacial level of about 280 ppm. The record kept in marine sediments tells us that 55 million years ago something happened which added a large amount of CO_2 to our atmosphere bringing about a sudden 5°C warming. The marine record also tells us that 250 million years ago the extinction of most of the organisms making up the Earth's biota led to a change in the way in which carbon was cycled. The five large dips in the ^{13}C to ^{12}C ratio in limestone which took place during the 800 to 540 million-year time interval tells us that the controls on the carbon throughput which have operated quite smoothly during the last 500 million years must have failed. Three of these lapses led to what is referred to as Snowball Earth episodes. Finally, we currently struggle to gauge the consequences and fate of CO_2 we are adding to the atmosphere as the result of burning fossil fuels.

Two examples of feedback loops which exert control on ocean carbon will help to understand the concept of feedback loops. The first involves the burial of $CaCO_3$ on the sea floor. Despite the fact that the surface ocean is several-fold supersaturated with respect to the mineral calcite, it does not spontaneously precipitate. Rather, it is manufactured by planktonic organisms. Chief among these are shell-forming plankton (foraminifera) and cage-forming algae (coccolithophoriads). In today's ocean, together they produce calcite at a rate roughly four times faster than its ingredients are being supplied to the oceans (see Fig.2-1). If this excess production were not somehow compensated, the ocean's inventory of Ca^{++} and $CO_3^{=}$ would be drawn down until the entire ocean was sufficiently undersaturated so that these organisms could no longer produce calcite houses. Clearly, the ocean must somehow compensate for this excess production. Since the surface ocean is highly supersaturated with $CaCO_3$, no way exists to regulate production of calcite carbonate hard parts. Instead, the balance between input and removal is accomplished by changing the fraction of the calcite raining onto the sea floor that dissolves. A feedback loop prevents imbalances. It involves adjustments in the carbonate ion concentration in the deep sea. The carbonate ion concentration is driven to that level where the excess falling into the deep sea dissolves. As the solubility of calcite increases with pressure (and hence with water depth), it is in the abyssal ocean that most of this dissolution takes place. This pressure dependence shows up prominently in the composition of recent deep sea sediments. At a depth of 2.5 km, open-ocean sediments consist of about 90 percent $CaCO_3$ and about 10 percent clay minerals and opaline silica. The clay minerals are supplied by dust and ash blown off the continents. The opal is produced in the surface ocean by diatoms. At a depth of 5.0 km, sediments contain no $CaCO_3$. The $CaCO_3$-rich sediment are referred to as foraminiferal ooze and the $CaCO_3$-free sediment as red clay. This difference reflects the fact that at 2.5 km the concentration product (i.e., Ca^{++} x $CO_3^{=}$) exceeds the saturation product for the mineral calcite. At 5 km the water is sufficiently undersaturated with respect to calcite that all the calcite raining to the sea floor dissolves. By contrast, the calcite which falls to the sea floor at 2.5 km depth is preserved. Somewhere below 2.5 km, the saturation boundary is crossed and dissolution commences. The deeper one goes, the more intense dissolution becomes until none of the raining calcite survives.

Now here's how the control system operates. If, for some reason not enough of the excess calcite production were to dissolve, the imbalance between output and input would draw down the ocean's $CO_3^{=}$ inventory. This would cause the saturation horizon to shoal.

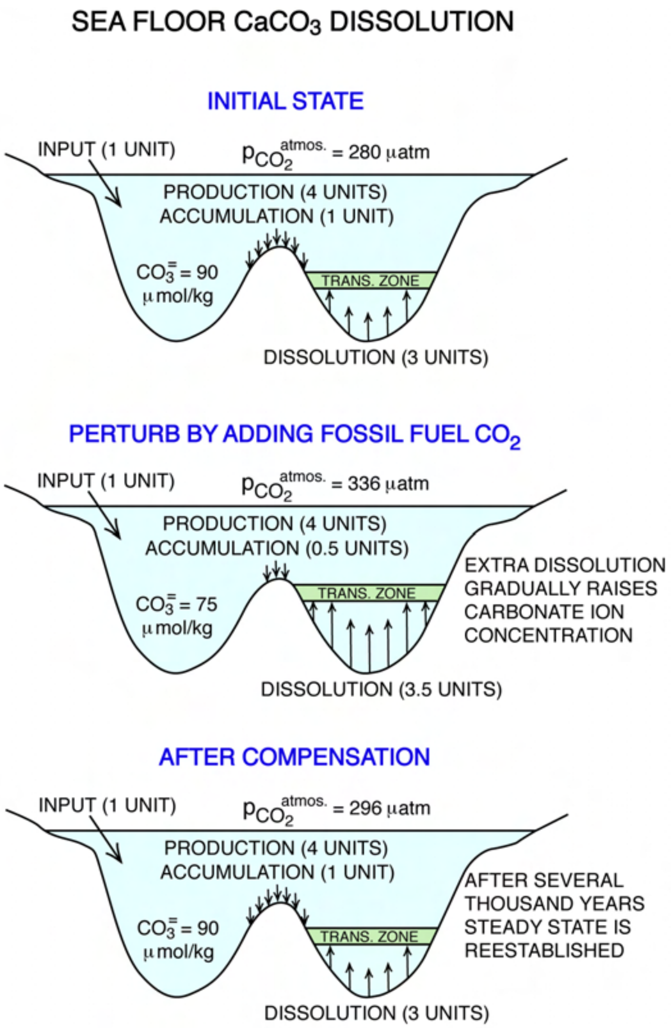


Figure 2-1. Currently marine plankton produce $CaCO_3$ at a rate about four times larger than the rate at which its ingredients are being supplied to the ocean. In order to compensate for this excess production, the carbonate ion concentration in the deep sea has stabilized at a level where three quarters of the calcite falls into water undersaturated with respect to calcite and dissolves. Keep in mind that the boundary between sediment rich in $CaCO_3$ and sediment devoid of $CaCO_3$ is not knife edged. Rather, it is a transition zone several hundred meters in thickness.

The fossil fuel CO_2 we are currently releasing to the atmosphere will eventually reach deep sea. As the uptake of CO_2 by the ocean involves a reaction with $CO_3^{=}$ ion to form two HCO_3^- ions, the result will be a decrease in the $CO_3^{=}$ ion content of ocean water. This will cause the transition zone to shoal and, consequently, a greater fraction of the raining calcite will dissolve. It will also increase the rate at which sedimentary $CaCO_3$ is dissolved. The excess dissolution will gradually replenish the lost carbonate ion, eventually returning the transition zone part of the way to its original depth. This will take several thousand years.

We have an analogue of such an event. At the boundary between the Paleocene and Eocene, a large amount of CO_2 was suddenly added to the atmosphere. When this CO_2 reached the deep sea, it lowered the CO_3 ion concentration leading to excess $CaCO_3$ dissolution. After being displaced down the water column, the transition zone would have gradually shoaled until it reached its pre-collision depth.

Consequently, a greater fraction of the sea floor would be subject to calcite dissolution. In this way the imbalance between delivery of ingredients and burial of the products would be eliminated. We know from the response of the ocean imbalances created by glacial cycles that any such imbalances are eliminated on the time scale of about 5 years (Fig. 2-2). One might ask why so short a time when the residence time of carbon in the ocean-atmosphere system is about 150,000 years. The answer is that the carbonate ion concentration in the deep sea (about 90 μmol/L) is only a small fraction of the total (about 2200 μmol/L).

The second example involves the feedback loop which controls the atmosphere's CO_2 content. To understand it we must consider the throughput of both calcium and carbon (Fig. 2-3). A portion of these elements reach the ocean as the result of dissolution of limestone exposed to continental weathering. As this contribution is removed as $CaCO_3$, it does not play a role in the control of the atmosphere's CO_2 content. The rest of the carbon is supplied by CO_2 which escapes from the Earth's interior in association with volcanic activity. The rest of the calcium is supplied by the chemical weathering of silicate minerals. As these latter inputs are also removed from the sea as $CaCO_3$, there must be a feedback loop which maintains an equality between the input of CO_2 and that of CaO. The amount of CO_2 released from the planet's interior is determined by processes occurring in the Earth's interior and hence is not influenced by what goes on at the surface. This being the case, the regulation must involve the calcium derived from silicate rocks. The key is that the CO_2 content of the atmosphere influences the rate of continental weathering. It does this by setting the Earth's temperature and rainfall. The warmer and wetter it is, the faster Ca is released from the silicate minerals in soils.

The feedback operates as follows. In order to be complete, account must be taken of the amount of carbon buried in sediments as organic material. As we shall see, based on carbon isotopes, over the course of the Phanerozoic, it has averaged about 20 percent of the total. In order to do the mass balance correctly, the amount of carbon buried in organic residues must be subtracted from the amount of CO_2 escaping from the planet's interior. If CO_2 emission were to

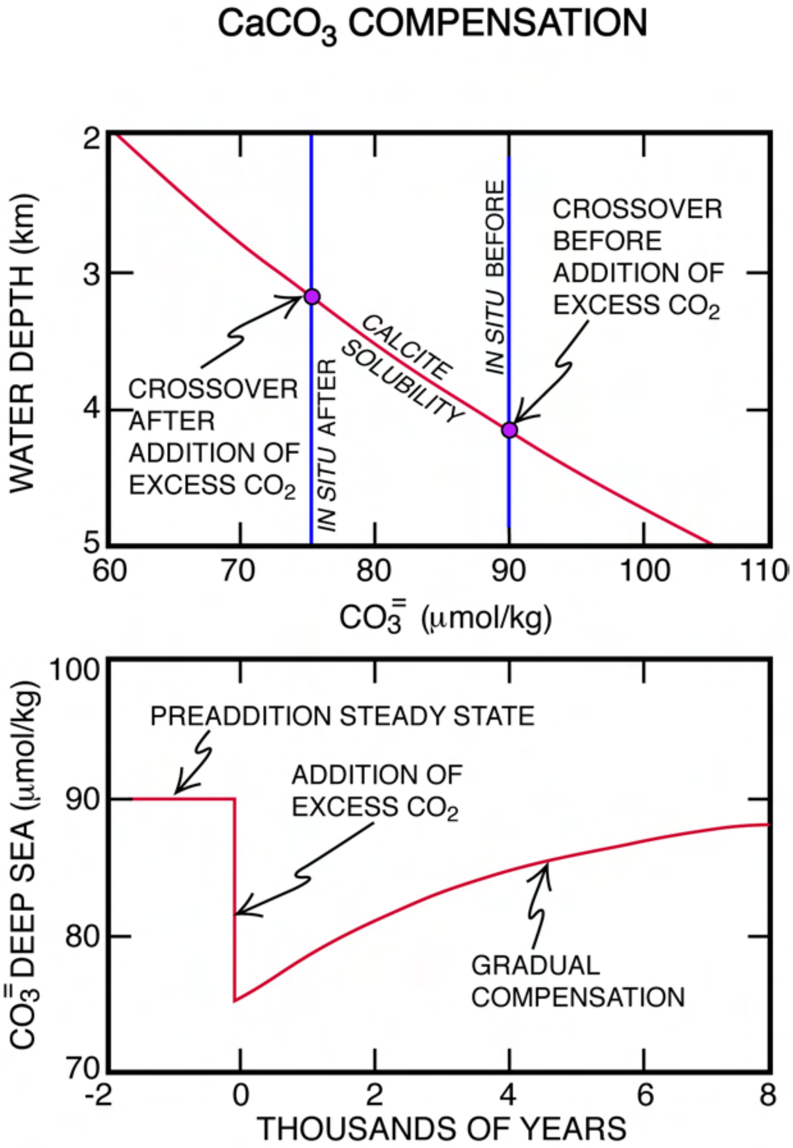


Figure 2-2. In today's Pacific Ocean, the in situ concentration of carbonate ion of deep water is nearly uniform with depth. But, as the solubility of calcite increases with pressure, a crossover from supersaturation to undersaturation occurs at a depth of about 4 km. If the ocean were to receive a jolt of extra CO_2 as it did during the PETM event, the $CO_3^=$ ion concentration would decrease causing the crossover to move to a shallower depth. As a result, there would be an increase in calcite dissolution. Over a period of thousands of years, the $CO_3^=$ ion concentration would build back up toward its pre-perturbation value.

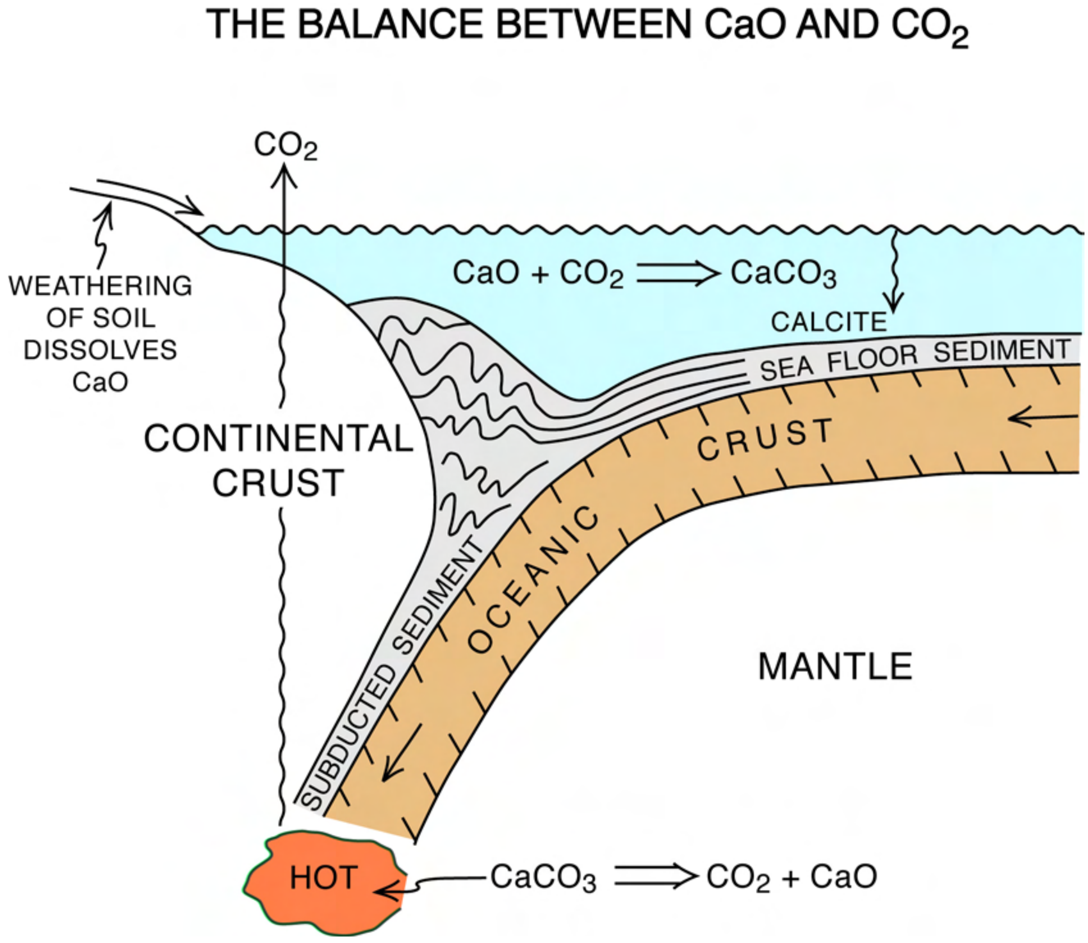


Figure 2-3. Shown here is a simplified version of Earth's carbon cycle. Instead of a complex of Na, Ca, Mg, Fe, Al, and Si oxides, continental crust is assumed to consist of only CaO. Weathering dissolves CaO. It is carried to the sea in rivers where it is deposited as $CaCO_3$ ($CaO + CO_2$). A portion of this $CaCO_3$ is subducted into the Earth's hot mantle where it decomposes to CaO and CO_2, completing the cycle.

As the CO_2 release from the Earth's interior involves tectonic processes which pay no attention to things happening at the surface, the match between the inputs of CO_2 and CaO must be maintained by adjusting the rate of delivery of CaO to the ocean. If CO_2 delivery were to exceed that of CaO, it would accumulate in the ocean-atmosphere reservoir. The consequent buildup of atmospheric CO_2 would warm and wet the planet increasing continental weathering rates. This buildup would continue until a match between CaO and CO_2 delivery was reestablished. Note that the cycle of organic carbon is not included in this simplification.

get ahead of calcium supply, CO_2 would build up in the atmosphere. This buildup would continue until weathering rate increased to the point where the balance between CaO and CO_2 delivery was restored. There are many scenarios by which such a mismatch might arise. An obvious one involves the rate of sea floor spreading. As CO_2 is emitted both at ridge crests and subduction zones, a change in the aggregate rate of seafloor spreading would alter the rate of addition of CO_2 to the ocean – atmosphere reservoir. Less obvious, but likely more important, is that CO_2 release depends on the amount of $CaCO_3$ and organic carbon contained in subducted marine sediment. Thermal dissociation of this material creates CO_2 which is carried back to the surface by volcanic activity. In today's configuration, subduction occurs largely along the Pacific Rim. The sediments in the deep Pacific basin are largely red clay. By contrast, 50 million years ago, much of the subduction occurred along the margins of the then Tethys Sea. Its sediments were rich in $CaCO_3$.

The geographic extent and location of basaltic provinces is also important. The reason is basalts weather far faster than other igneous rocks. Further, when located in the warm and wet tropics, basalts weather even more rapidly. So it is not only changes in CO_2 delivery induced by volcanic activity that perturb the system, but also the size and geographic positioning basaltic provinces which alter the rate of delivery of calcium. Hence it is not surprising that there have been variations in the atmosphere's CO_2 content. They were inevitable!

An interesting aspect of this has to do with the evolution of rooted plants. Roots aid in chemical weathering in two ways. First, they transport organic matter deep into the soil where it is converted to CO_2 gas. The acidification of soil water by respiration CO_2 accelerates weathering. Second, rootlets secrete organic compounds which nourish symbiotic bacteria capable of breaking down soil minerals. Thus everything else being equal, as rooted plants evolved, the required supply of matching calcium could be accomplished at ever lower atmospheric CO_2 contents.

Both of these examples involve the interaction between the cycles of the elements carbon and calcium. Hence one might think that they might interact with one another. But as they operate on far different time scales, this is not a consideration. As we have already seen, imbalances between the delivery of the ingredients for $CaCO_3$ and the burial of $CaCO_3$ are compensated for on the time scale of thousands of years. By contrast, the adjustment of the supply of CaO to match that of CO_2 takes place on a time scale of millions of years.

A few additional control systems need mentioning. The carbon isotope record in limestone tells us that over the last 500 million years, the partitioning between the amount of carbon leaving the ocean as organic matter and that leaving as calcium carbonate has remained remarkably constant. On the average, about 20 percent of the carbon has been buried as organic matter and about 80 percent as $CaCO_3$ (Fig. 2-4). This near constancy is puzzling in that, at least during the Cenozoic era, sites of deposition of these two carbon carriers have been separated. Organic matter is stored in rapidly accumulating sediment (i.e., river deltas). Calcium carbonate is stored primarily in deep sea sediments. Further, as carbon cycles through the ocean on a time scale of 200 or so thousand years, the control must operate on a geologically short time scale. During the last 50 million years, ocean carbon has turned over some 250 times. For each of these cycles, the 20 percent – 80 percent partitioning has been maintained.

So what is it that maintains this partitioning? The answer is that I don't know. The best guess would be that it involves a link to O_2. For every mole of carbon stored in sediment as organic matter, one mole of O_2 remains behind in the atmosphere. The more O_2 in the atmosphere, the more effective it is in invading isolated sedimentary niches. Today photosynthesis produces an amount of O_2 equal to that in the atmosphere each one thousand years. Hence this feedback could certainly operate rapidly enough. However, as the preservation of organic material in deltas is made possible by rapid burial, it is not clear how effective such an O_2 feedback would be.

There is, however, an escape hatch from this dilemma. It has to do with the assumption

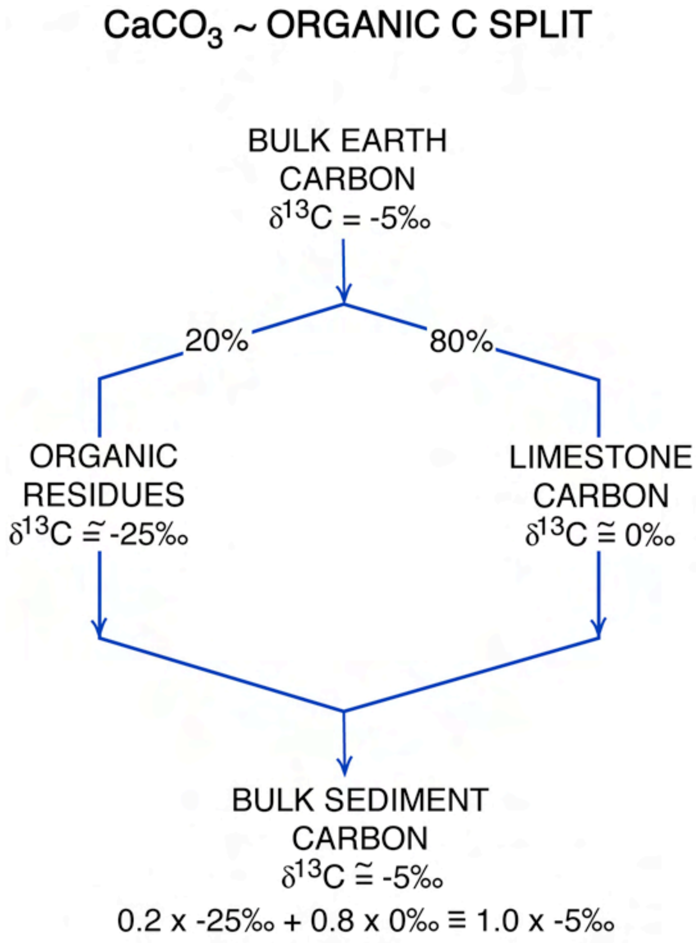


Figure 2-4. The near constancy of the carbon isotope ratios in limestone suggests that over the last 500 million years roughly 80 percent of the carbon added to the ocean-atmosphere reservoir was removed as $CaCO_3$. The remaining 20 percent was stored as organic residues. As carbon currently resides in the ocean for only about 0.2 million years, some feedback must maintain the 80-20 proportions. An obvious candidate is the O_2 content of the atmosphere. If the proportions were to change, so also would the O_2 content of the atmosphere. The reason is that for every mole of organic matter stored in the sediments, one mole of O_2 is left behind in the atmosphere. However, as most of the organic matter is stored in rapidly deposited sediments such as deltas, it is not obvious how an atmospheric O_2 feedback could serve to adjust the preservation of organic matter.

This scenario is marred by the fact that it doesn't include the contribution of recycled limestone ($\delta^{13}C$ ~0‰). If half the carbon supplied to the ocean were contributed by recycled limestone, then only about 10 percent of the carbon removed from the ocean would be in the form of organic matter. In this case, a 1% change in the $\delta^{13}C$ of limestone would correspond to a 30 percent change in the fraction of organic matter. Hence, the contribution of organic matter could have changed significantly.

that the isotopic composition of the input carbon is that for bulk earth carbon (i.e., ~-5‰). Although this is a good choice for the carbon coming from the Earth's interior, it is not for the carbon weathered from limestones (i.e., ~0‰). If, for example, their contributions were about equal, then the fraction of carbon buried in organic residues would have to be 10 rather than 20 percent (see Fig. 2-5). Were this the case, then the small variations in $\delta^{13}C$ observed for limestone would permit sizable variations in the fraction of carbon buried as organic matter. I think that this is likely the answer.

This raises yet another consideration, namely, the link between the cycles of sulfur and carbon. If the rain rate of organic matter to the deep sea were to exceed the supply of O_2 to the deep sea, sediments would become anoxic. As a result, there will be no burrowing organisms to consume the rain of organic matter. Under these conditions, bacteria capable of utilizing dissolved sulfate rather than dissolved O_2 as an oxidant source will come to fore. As a source of energy, they reduce $SO_4^{=}$ to $S^{=}$. The sulfide reacts with iron forming minerals such as pyrite (FeS). Even after bacteria have consumed all the available SO_4, they still can derive energy by decomposing organic matter to form CH_4 and CO_2. However, as anaerobic bacteria are not as effective in decomposing organic matter as aerobic organisms, a significant portion of the organic matter will accumulate in the sediment and its matching O_2 will accumulate in the atmosphere. So, it stands to reason that the O_2 content of the atmosphere serves to modulate the extent of decomposition of organic matter.

There is one more player in this complex of control systems, namely, the element phosphorus. Its availability limits plant growth in the surface ocean. In today's ocean, there is an over-abundance of dissolved inorganic carbon relative to phosphorus. Hence carbon never limits the manufacture of organic matter. Although fixed nitrogen co-limits productivity, among the various species of planktonic organisms there are those capable of converting the N_2 gas into utilizable NO_3. Were its availability to run short, these nitrogen fixers would gain an ecologic advantage and promptly eliminate the deficiency. Another feedback loop!

So, of the big three elemental constituents of marine organisms, it is phosphorus

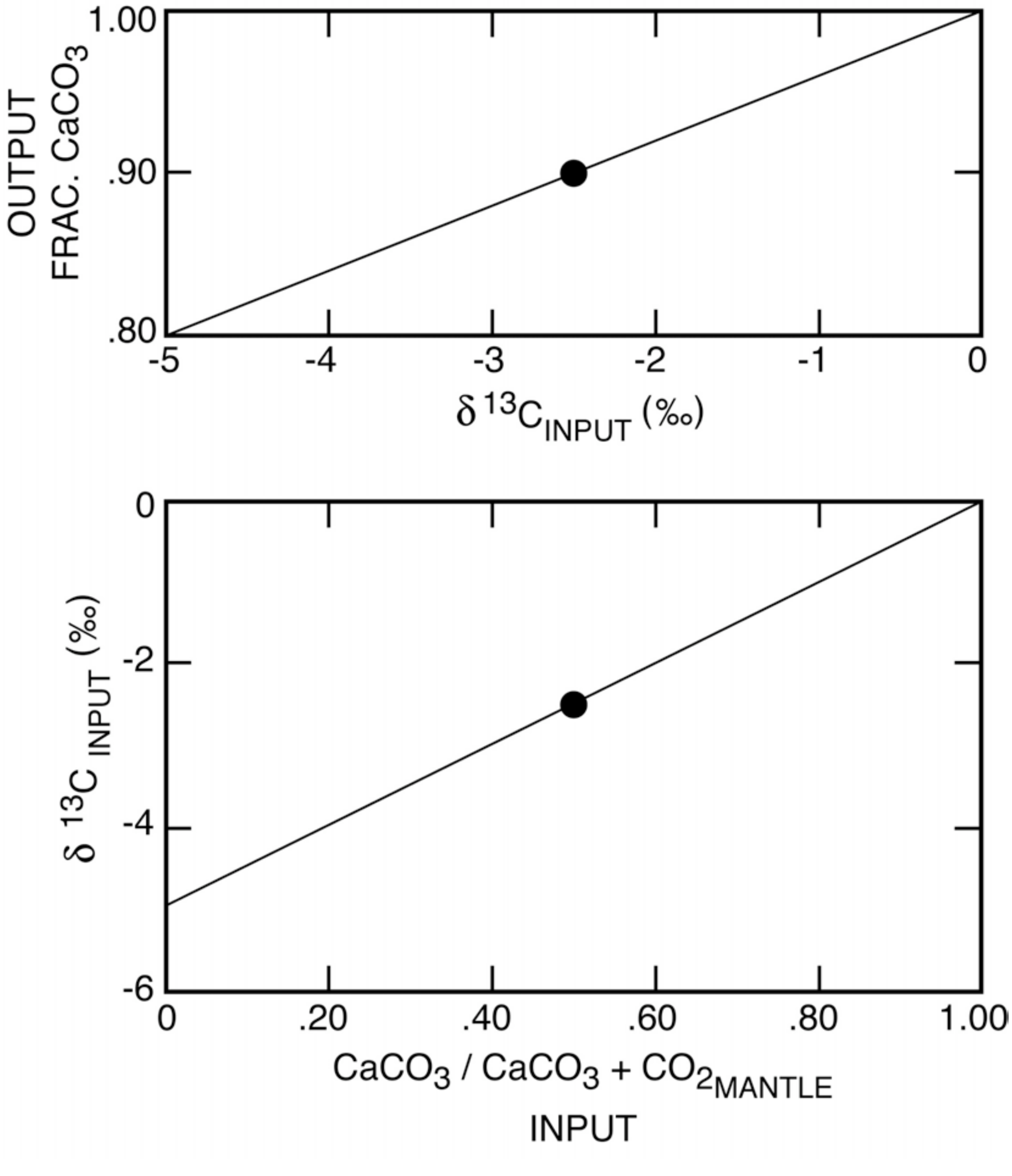


Figure 2-5. The $\delta^{13}C$ of carbon added to the ocean-atmosphere reservoir depends on the relative contributions of limestone and volcanic CO_2. If the two sources of carbon were equal, then the input $\delta^{13}C$ could be -2.5 per mil rather than the usually assumed value of -5 per mil. If so, only 10 percent of the output would be in the form of organic matter. The importance of this is that it would allow the organic contribution to vary over a larger range without creating unacceptably large variations in the ocean's $\delta^{13}C$.

that limits growth. No way exists for the marine ecosystem to enhance its supply. Rather it is set by delivery from the continents. Although marine organisms can't enhance the supply of phosphorus, they can influence its residence time in the sea. Today's marine ecosystems are very good at this. The average PO_4 unit remains in the oceans for several tens of thousands of years. During its residence, it is taken up and released several thousand times before, by chance, becoming buried in sediment.

The cycle of PO_4 is linked to that of O_2 (see Fig. 2-6). The reason is that the higher the ratio of PO_4 to O_2, the more likely it is that parts of the ocean's interior will become anoxic. The logic is as follows. Water descending into the deep sea has an O_2 content close to saturation. In today's ocean, new deep water carries about 350 μmol/liter of O_2. The PO_4 content of ocean water averages about 2 μmol/liter. As 175 moles of O_2 are utilized for each mole of PO_4 released during respiration, were all the PO_4 upwelling to the surface to be utilized by plants and sent to the abyss as organic matter, the deep ocean O_2 concentration would dip to zero. This does not happen in today's ocean because about two thirds of the PO_4 upwelled in the Southern Ocean is not utilized. It is returned to the deep sea in dissolved form rather than bound in organic matter.

Nevertheless, the O_2 content of deep water in the mid-depth northern Pacific dips dangerously close to anoxia (20 μmol/liter O_2 content). I suspect that the reason that no large portion of the deep ocean is anoxic is that, for each mole of organic matter oxidized by SO_4 (or buried without oxidation), one mole of O_2 would build up in the atmosphere. This would raise the O_2 to P ratio until oxic conditions were restored. Yet another feedback loop! It is interesting in this regard to note that throughout the Cenozoic benthic foraminifera shells are present in all open ocean sediments. This tells us that there have been no episodes of open ocean anoxia. I say 'open ocean' because anoxic waters are to be found beneath zones of intense coastal upwelling.

So far, all the examples presented here involve those constituents in the ocean that are utilized by living organisms. Magnesium is an example of one that is not. It is supplied

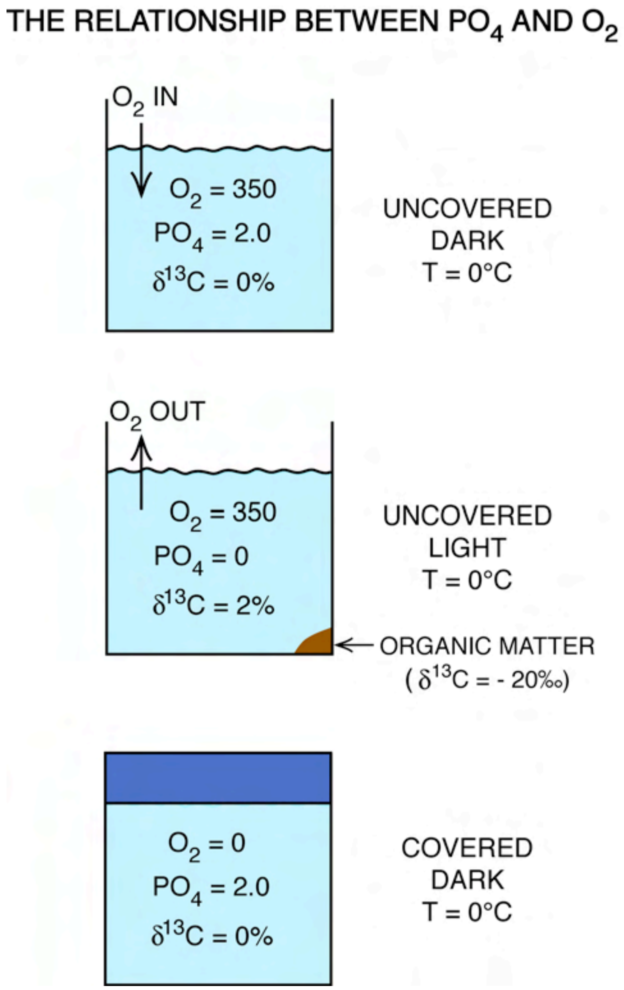


Figure 2-6. The ratio of atmospheric O_2 to oceanic PO_4 sets the likelihood that parts of the deep ocean will become anoxic. Shown here is a simple thought experiment that demonstrates this relationship. If a bucket of seawater from the deep Pacific Ocean were to be placed in a cold and dark basement, it would absorb O_2 from the air. The saturation concentration at 0°C would be 350 μmol/liter. If the lights were turned on, algae in the water would produce organic matter until the PO_4 ran out. If the initial PO_4 concentration were 2 μmol/liter, 350 μmol/liter of O_2 would be produced. But, as there is no cover on the bucket, the extra O_2 would leak out. If a cover was then placed on the bucket sealing it off from the atmosphere, bacteria in the water would eventually oxidize the organic material. As 175 micromoles of O_2 is required to oxidize organic matter containing one micromole of PO_4, the O_2 would be entirely consumed. As today's ocean has an average PO_4 concentration of 2 μmol/liter and newly formed deep water has an O_2 content of 350 μmol/liter, one might think that parts of the deep ocean would be anoxic. But even though the O_2 content in the deep North Pacific drops to 20 μmol/liter, none of the deep open ocean is anoxic. The reason is that in today's ocean not all the PO_4 which reaches the surface is utilized. The unused portion is carried back down with newly formed deep water. Further, if a portion of the deep sea were to become anoxic, the O_2 content of the atmosphere would rise until it became oxic.

to the ocean by the chemical weathering of silicate and dolomitic rocks. Today it is removed largely by ridge-crest hydrothermal circulation. We know this because the hot water exiting ridge crest vents contains no magnesium. Based on its ocean inventory and the amount carried to the ocean in rivers, magnesium is being replaced on a time-scale of roughly five million years. Were ridge crest removal the only contributor, then its concentration in the seawater would depend solely on the rate of sea floor spreading. The faster the spreading, the more water passed by hot rock and the faster magnesium would be removed. Were it the whole story, then as spreading rates have not changed greatly, its concentration would not be expected to have changed. But, as we shall see, its concentration has doubled over the past 50 million years. The likely reason is that the removal of magnesium by the formation of dolomite has been largely shut down as the result of a lowering of sea level.

The most slowly replaced constituents of sea water are sodium and chloride (see Fig. 2- 7). One source of both is the dissolution of old salt deposits exposed by chance at the Earth's surface. One sink is the formation of salt deposits in arms of the ocean cut off from communication with the whole. Another important storehouse for chloride is brines which fill the pores of deeply buried sediments. As shuttling back and forth between sediment and ocean is largely episodic, we can only say that the turn over time could be as long as a billion years.

CONSTITUENT	CHEMICAL FORM	CONCENTRATION mol/L	RESIDENCE TIME years
IRON	Fe^{+++}	MINISCULE	$\sim 1 \times 10^3$
OXYGEN GAS	O_2	3×10^{-4}	$\sim 1 \times 10^3$
NITROGEN	NO_3^-	3×10^{-5}	$\sim 3 \times 10^3$
PHOSPHORUS	PO_4	2×10^{-6}	$\sim 2 \times 10^4$
CARBON	$CO_2 + HCO_3^- + CO_3^=$	2×10^{-3}	$\sim 2 \times 10^5$
LITHIUM	LI^+	2×10^{-5}	$\sim 6 \times 10^5$
CALCIUM	Ca^{++}	1×10^{-2}	$\sim 1 \times 10^6$
STRONTIUM	Sr^{++}	9×10^{-5}	$\sim 5 \times 10^6$
MAGNESIUM	Mg^{++}	5×10^{-2}	$\sim 5 \times 10^6$
BORON	$H_3BO_3 + H_4BO_4^-$	4×10^{-4}	$\sim 1 \times 10^7$
SODIUM	Na^+	5×10^{-1}	$\sim 3 \times 10^8$

Figure 2-7. Concentrations and residence times of important constituents of sea salt. The residence times are based on the ratio of the ocean inventory to either the rate of addition or the rate of removal. They are all approximate because 1) they assume that the constituent is at steady state and 2) the difficulty in establishing the required fluxes.

References for Chapter 2

Berner, R. A., A. C. Lasaga, and R. M. Garrels (1983), The carbonate-silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years, *Am. J. Sci.*, *283*, 641-683.

Broecker, W. S. (1970), A boundary condition on the evolution of atmospheric oxygen, *J. Geophys. Res.*, *75*, 3553-3557.

Broecker, W. S. (1971), A kinetic model for the chemical composition of sea water, *Quaternary Res.*, *1*, 188-207.

Walker, J. C. G., P. B. Hays, and J. F. Kasting (1981), A negative feedback mechanism for the long-term stabilization of Earth's surface temperature, *J. Geophys. Res.*, *86*, 9776-9782.

Chapter 3

Proxies

Some of our best insights into what controls the flow of carbon through the ocean- atmosphere system comes from perturbations experienced in the past. These perturbations are reconstructed using what we call proxies. Except for the gases trapped in polar ice, we must resort to stand-ins for the properties of interest. As such, the interpretation of what they are telling us is rarely unambiguous. But, by combining the information gleaned from a number of them, we have been able to learn a surprising amount about the history of ocean-atmosphere chemistry. In the sections which follow, I introduce the set of proxies that I deem most useful.

First, and most important, is the reconstruction of the atmosphere's CO_2 content. Measurements of the CO_2 concentration in the air trapped in Antarctic ice precisely document the record for the last 0.8 million years (see Fig. 3-1). Attempts are currently underway to find even older ice suitable for this purpose. But to go further back in time we must resort to CO_2 proxies.

The Boron Isotope Proxy

The next step back in time is based on the isotopic composition of boron contained in the calcitic shells manufactured by foraminifera (see Fig. 3-2). The ratio of ^{11}B to ^{10}B in these shells is set by the pH of the water. In seawater the neutral boron species, $B(OH)_3$ has a 20 per mil larger ^{11}B to ^{10}B ratio than the charged species $B(OH)_4^-$. As the proportions of these two species change with pH, so also must their isotopic compositions. At pHs greater than 11, almost all the boron is in the charged form. So, $B(OH)_4^-$ has the same isotopic composition as bulk seawater boron. At pHs below 7, almost all the boron is in the neutral form. So $B(OH)_3$ has the same isotopic composition as bulk seawater boron. At a pH of 8.7, the amounts of the two species are equal. The $H(BO_4^-)$ has an ^{11}B to ^{10}B ratio about 10 per mil lower than that of bulk boron and the $B(OH)_3$ has a ratio about 10 per mil higher. The paleo pH proxy is based on the assumption that

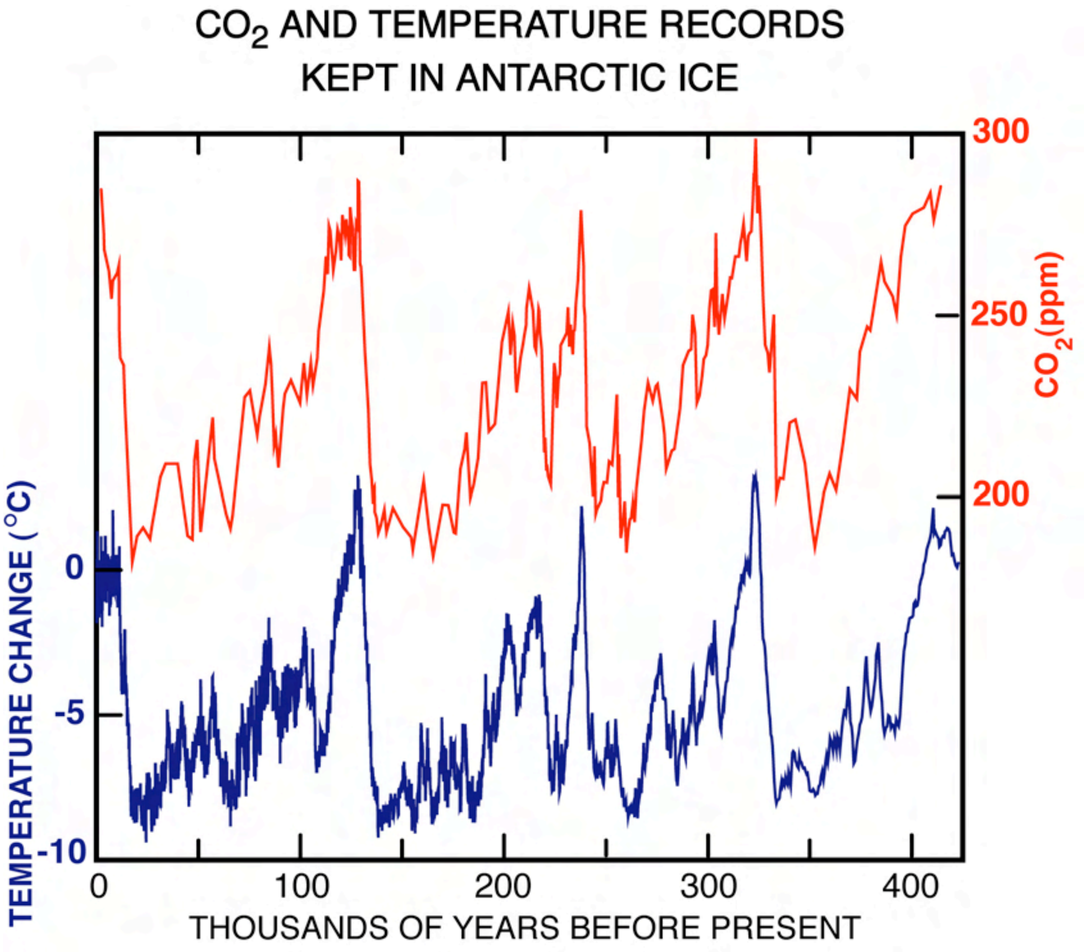


Figure 3-1. Records of CO_2 and air temperature for the last 400,000 years from an ice core drilled by Russian scientists at the Vostok Camp site on the Antarctica polar plateau. The CO_2 record generated by Jerome Chappellaz is based on measurements on air trapped in bubbles in the ice. The temperature record is derived from deuterium to hydrogen ratios measured by Jean Jouzel in the ice itself. Both geochemists work in France. As the air bubbles closed off at a depth of about 80 meters and the ice accumulates at only a few centimeters per year, a time offset of several thousand years separates these two records. In order to compare the two records, an adjustment must be made for the duration of this offset. As the exact magnitude of this adjustment remains uncertain, careful consideration must be given to the phasing of the interglacial peaks.

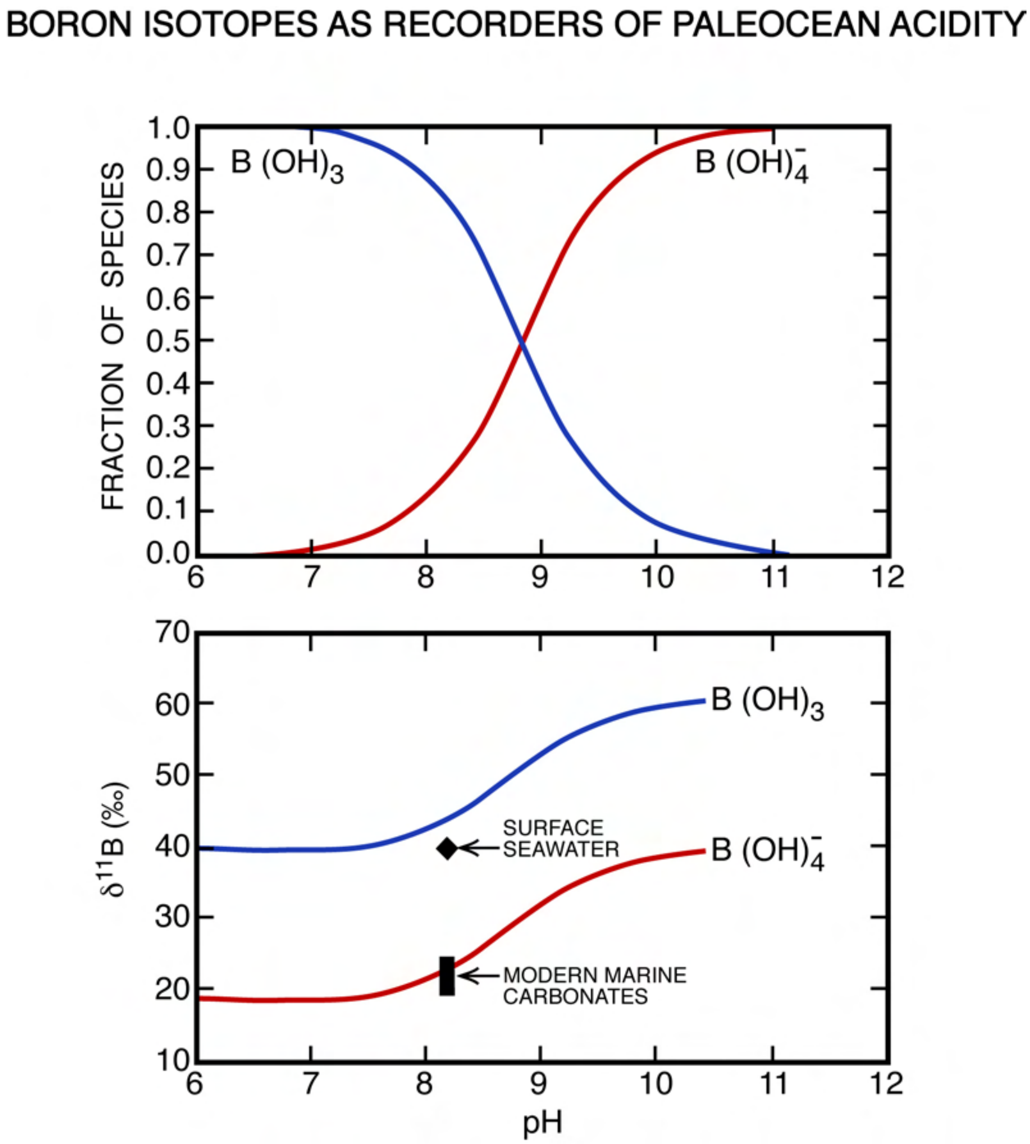


Figure 3-2. As first shown by Gary Hemming, the isotopic composition of the boron contained in the shells of planktonic foraminifera serves as a proxy for surface ocean pH. It is based on 20 per mil difference in the isotopic composition of HBO_3^0 and HBO_4^- in seawater. As the pH increases from 7 to 11, HBO_4^- goes from just a trace to the dominant species. Hence, its δ^{11}B goes from about 20 per mil to about 40 per mil. As only the charged boron species substitutes in the calcite, the isotopic composition of the boron-contained calcite serves as a paleo pH proxy. Assuming that the DIC concentration in surface water has not changed significantly, the pH can be converted to CO_2 concentration. As past water temperatures can be reconstructed from the magnesium content of the shell calcite, the CO_2 concentration can be converted to a CO_2 partial pressure.

only the charged species $B(OH)_4^-$ is incorporated in the shell calcite.

In order to convert the reconstructed pH to pCO_2, one other component of the carbon system must be known. For the last few million years, it is safe to assume that the total dissolved inorganic carbon content (i.e., DIC) of the surface ocean has been sufficiently constant to permit the CO_2 content of the water to be calculated from its pH. In order to convert the CO_2 content of the water to the CO_2 partial pressure in the water, the temperature of the water must be known. Paleo temperatures based on oxygen isotope clumping, Mg to Ca ratios in planktic foraminifera and on the composition of alkenones in coccoliths are used for this purpose. Further, as in in today's ocean the CO_2 partial pressure in oligotrophic surface water is close to that in the atmosphere, the boron isotope ratio in foraminifera shell manufactured in these waters serves as a proxy for the partial pressure of CO_2 in the atmosphere.

Lamont-Doherty's Bärbel Hönisch has tested this method by comparing ^{11}B to ^{10}B derived CO_2 estimates with the atmospheric CO_2 changes directly recorded in Antarctic ice. She succeeded in reproducing the main features of this record. But, as the error bars on her measurements (±15 μatm) are much larger than those for CO_2 trapped in ice (±2 μatm), she did not attempt to capture the details. Based on her success in reproducing the CO_2 record kept in the Antarctic ice, Hönisch pushed back in time. She showed that for the last four million years the atmosphere's CO_2 content has remained within the range recorded in Antarctic ice (i.e., 240 ± 40 μatm).

As the mean residence time of boron in the ocean is about 10 million years, on times of more than a few million years its isotopic composition could have changed. Hence, it is important to have a proxy for the bulk isotope composition of marine boron. Two approaches have been taken. The first is to measure the ratio in boron in fluid inclusion contained in marine halite. These measurements suggest a steep increase in the ratio (7 per mil in the last 18 million years and 15 per mil since the Devonian). However, measurements carried out on planktonic shells 35 million years in age are in sharp disagreement. Based on reasonable assumptions regarding how much the pH of the ocean could have changed, the conclusion is that, instead of changing by 8 or so per mil over the last 35 million years as the fluid inclusion results suggest, the change has been only about 3 per mil.

But even in the absence of a reliable reconstruction of the ocean's boron isotope composition, the method is still useful for documenting short-term changes in the atmospheric CO_2 partial pressure. At pH in the 8.2 range, for each 0.3 pH unit change, the CO_2 partial pressure changes by roughly a factor of two. This constraint is of particular interest because Earth temperature depends on the logarithm of the atmosphere's CO_2 content. Ocean-atmosphere models suggest that in today's world each doubling of CO_2 would warm the planet about 3°C. But it must be kept in mind that a pH below 8.0 and at pH above 8.5, the change in pH with $\delta^{11}B$ becomes ever larger (see Fig. 3-2).

The Alkenone ^{13}C Proxy

The next step back in time is based on the ^{13}C to ^{12}C ratio in the organic material made by marine plankton (Fig. 3-3). As originally shown by growth experiments conducted by New Zealand's Chris Hendy, the $\delta^{13}C$ of fresh water algae varies with the CO_2 content of the water in which they were grown. The higher the CO_2 content, the larger the depletion in the algae's ^{13}C to ^{12}C ratio. In an attempt to determine whether this was the case for bulk plankton recovered from surface ocean, UCSC's Greg Rau found that, although for waters colder than 15°C there was a good match with the Hendy's lab trend, for tropical plankton the extent of fractionation deviated from the cold water trend. It turns out that the PO_4 content of the growth water and the size of the cell influence the magnitude of the ^{13}C–^{12}C separation.

To understand this requires a discussion of why the fractionation factor depends on the CO_2 concentration. The magnitude of the ^{13}C–^{12}C separation is set by the competition between the isotope separation that occurs as CO_2 diffuses through the cell wall and that which occurs as it reacts with rubisco (the enzyme which converts CO_2 to sugar) (Fig. 3-4). The cell wall fractionation is small (i.e., about 4‰) and the rubisco fractionation is large (i.e., about

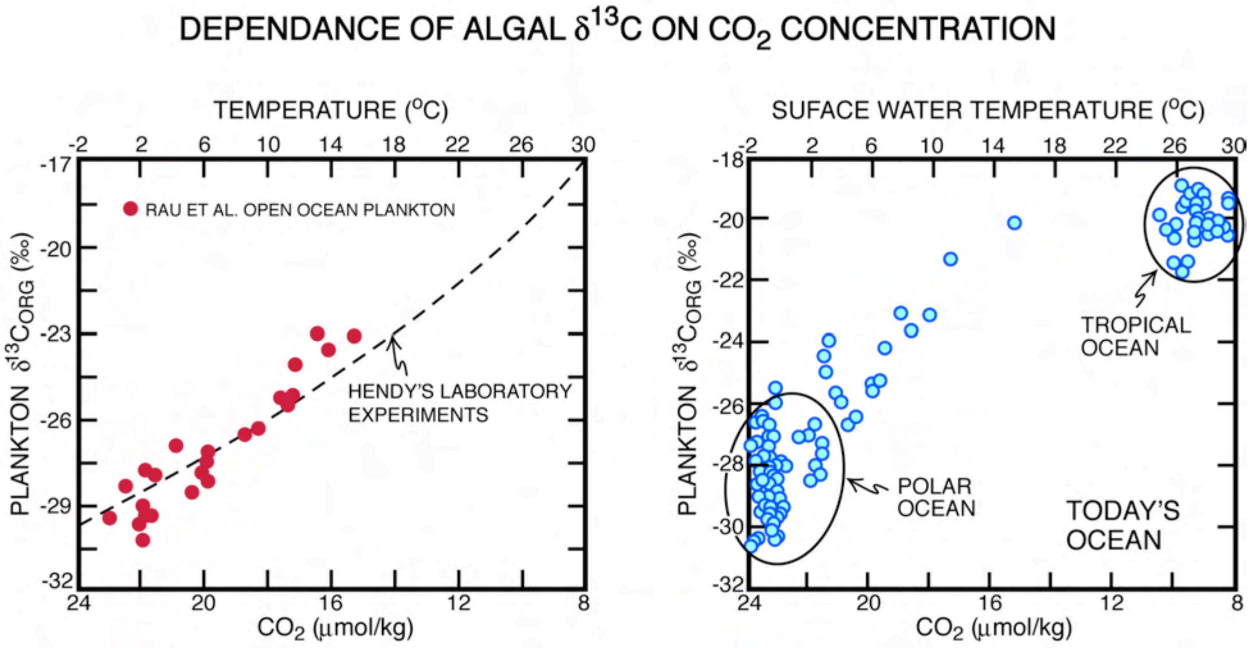


Figure 3-3. Laboratory growth experiments carried out by New Zealand's Chris Hendy first demonstrated the dependence of the $\delta^{13}C$ for algae on the CO_2 content of the water. The University of California's Greg Rau made measurements on marine plankton to determine whether they followed the Hendy trend. For plankton waters with temperatures less than 15°C, the slopes do match. However, difference between the isotopic composition of tropical plankton and polar plankton (i.e., about 8 per mil) is smaller than that expected from Hendy's experiments (i.e., about 13 per mil).

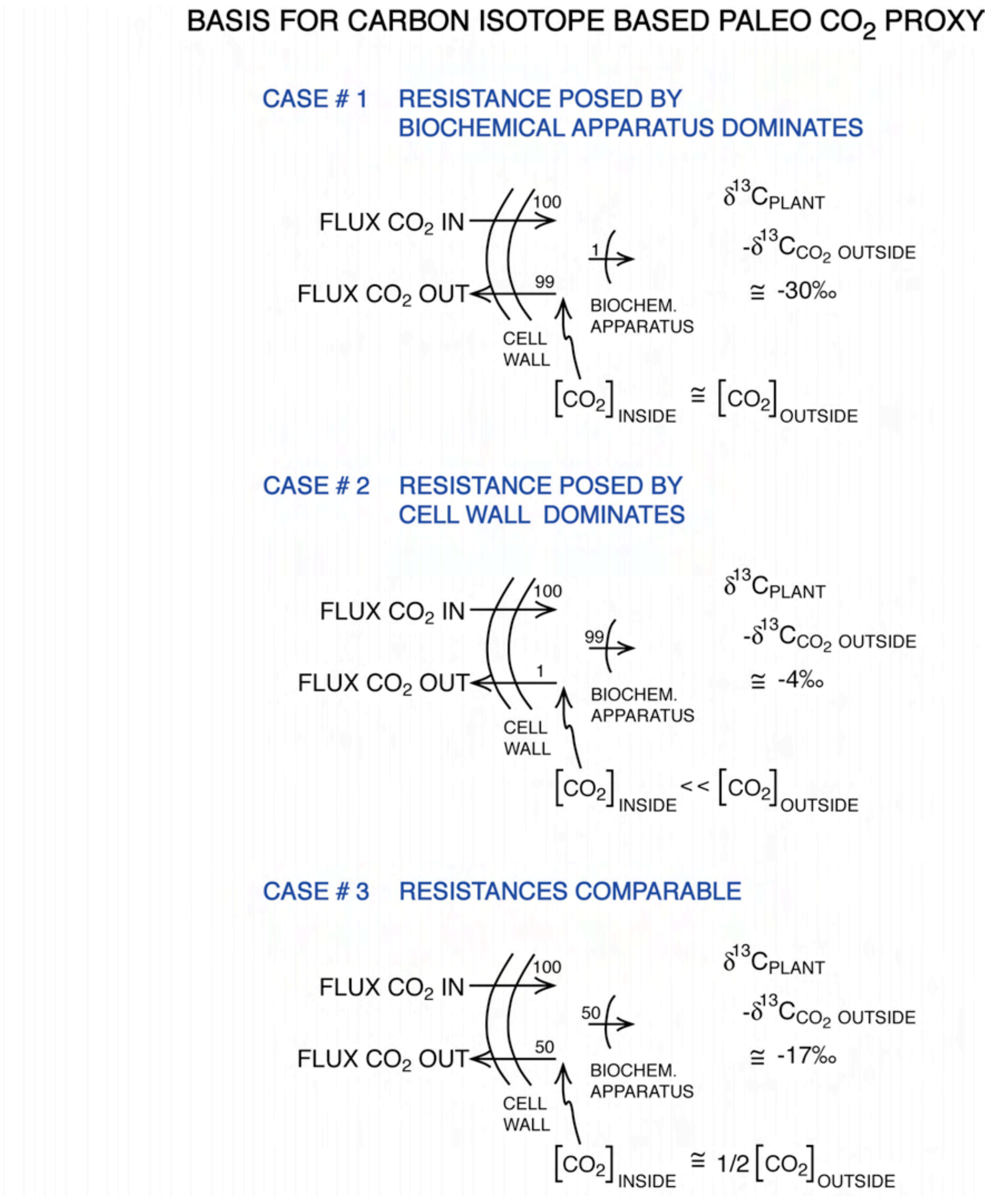


Figure 3-4. The carbon isotope fractionation in C-3 aquatic plants depends on the CO_2 content of the water in which they grow. The higher the CO_2 content, the more important is the discrimination against the heavy isotope (i.e., ^{13}C) during the conversion of CO_2 to sugar. This biochemical discrimination is far larger than that which occurs during passage through the cell wall. Thus the $\delta^{13}C$ of algal tissue varies with the CO2 content of the water. The higher it is, the larger the ^{13}C deficiency in the tissue.

30‰). If the rate of passage of CO_2 back and forth through the cell wall is rapid compared with the rate of its reaction with rubisco, then the fractionation will approach 30‰. If the opposite is the case, the fractionation will approach 4‰. The higher the CO_2 content of the water, the more rapidly CO_2 enters the cell and the larger the isotope fractionation (see Fig. 3-4). As the uncertainty of paleo CO_2 partial pressures obtained in this way is on the order of 50 µatm, comparison with the Antarctic ice core record would not be particularly fruitful. In any case, to my knowledge it hasn't been done.

The reason that the carbon isotope fractionation is influenced by the PO_4 content of the water is that it influences the rate of CO_2 uptake by the enzyme rubisco. The more phosphate, the faster the CO_2 reacts. Hence increased PO_4 reduces the extent of carbon isotope fractionation. In an attempt to minimize the influence of PO_4, CO_2 reconstructions are based on organic material formed in oligotrophic surface water, (i.e., water with very low PO_4 content).

Cell morphology influences the competition between the two uptake resistances. To minimize this complication, measurements are made on organic compounds manufactured only by the coccolithophorid Emiliani huxleyi. Coccolithophoriads are also favored for, unlike foraminifera, they calcify exclusively in the surface mixed layer. This is important because the CO_2 content of seawater increases rapidly below the base of the mixed layer. However, the use of this proxy is limited to the last 38 million years (no E. huxleyi before that time).

The ^{13}C measurements are made on a specific compound rather than bulk organic material. The reason is that each of the compounds making up organic matter has a slightly different ^{13}C to ^{12}C ratio. Alkenones are chosen because they are manufactured exclusively by Emiliani huxleyi. Further, as these organisms live in the sunlit upper ocean, complications related to the increase in respiration CO_2 with depth in the thermocline are avoided.

In recent years, a more serious criticism has been brought forward. It has to do with the use of bicarbonate ion. As there is more than 100 times more bicarbonate than CO_2 in surface seawater, one might ask why plants don't take advantage of this great abundance. If, as the records suggest, atmospheric CO_2 has decreased during the course of the Cenozoic, perhaps the use of bicarbonate has increased. If so, then the CO_2 reconstructions obtained in this way may be seriously biased.

The Stomatal Resistance Proxy

Beyond 38 million years, three CO_2 approaches have been proposed. Yale's Bob Berner pioneered the use of chemical mass-balance modeling to constrain how CO_2 has changed. As these reconstructions require a large number of questionable assumptions, I view them as marginal in value. Rather, reconstructions must be based on proxies. One such approach involves the frequency and size of leaf stomata. Although there is certainly a dependence on CO_2, this approach has been severely criticized and hence marginalized. Fortunately, a breakthrough has occurred which changes this situation. By making use of the $\delta^{13}C$ of the leaf material, Franks et al. (2014) have replaced the conventional approach with one they refer to as the stomatal conductance method. It is based on physics rather than correlation. Further, rather than being limited to a single species, it works equally well on leaves or needles from any C-3 plant. As C-3 plants evolved 200 million years ago, it offers a far longer record of atmospheric CO_2 content.

The Soil Calcite Proxy

Another approach involves the carbon isotope composition of soil $CaCO_3$ (Fig. 3-5). The idea, first proposed by University of Utah's Thure Cerling, is based on the fact that the CO_2 in soils pores has two sources. One is the atmospheric CO_2 in the air which is present in pores. The other is the CO_2 generated within the soil by respiration. As atmospheric CO_2 has a $\delta^{13}C$ of about -6 per mil and respiration CO_2 a $\delta^{13}C$ of about -24 per mil, the $\delta^{13}C$ of the soil CO_2 depends on the ratio of these two contributors. For example, if half the CO_2 were atmospheric and half respiration, then the $\delta^{13}C$ of soil CO_2 would be -18 (half way between -6 and -24‰. As the pre-industrial atmospheric pCO_2 was 280 μatm and the pCO_2 generated by soil respiration is thousands of μatm, the $\delta^{13}C$ of soil gas is currently close to that for

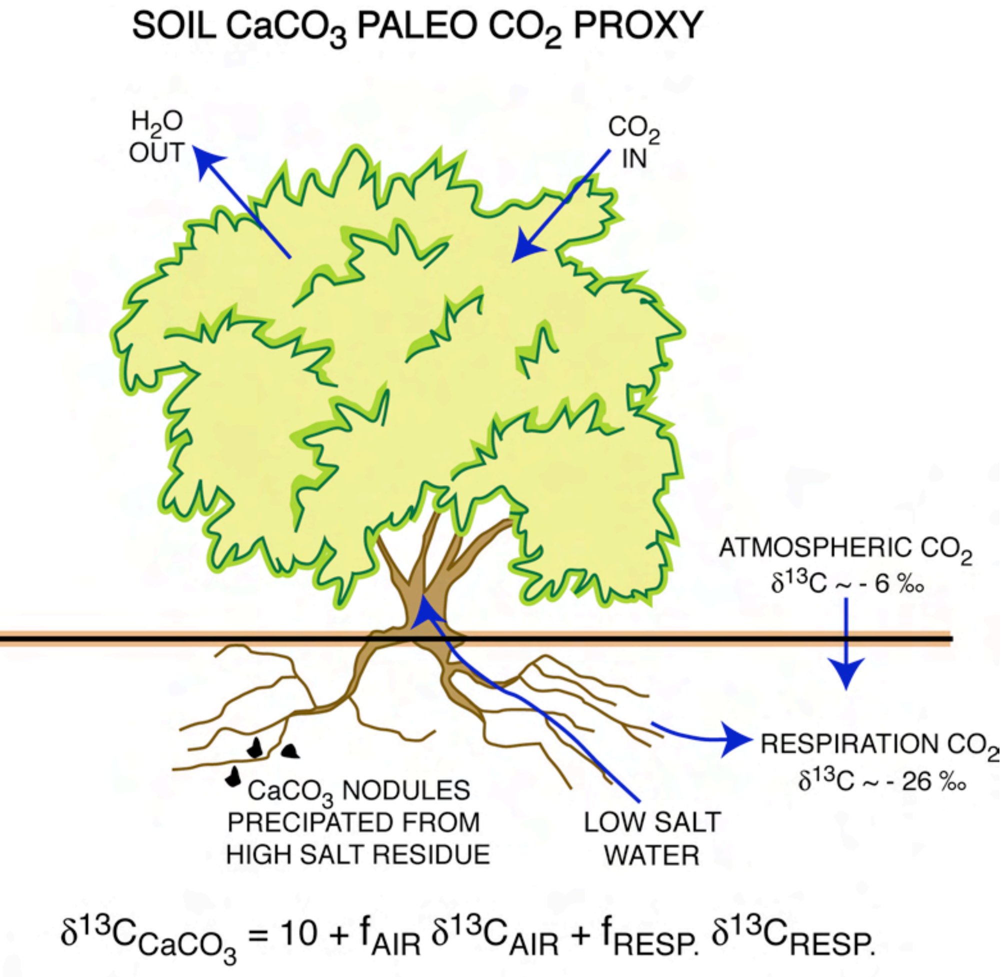


Figure 3-5. Unlike forests where a sizable fraction of the rainfall drains through the soil into the underlying ground water table, in dry lands this does not happen. Rather, the water entering soils is efficiently sucked up by plants and transpired. To avoid salt buildup in their leaves the roots of the plants have the capability to desalt the water they take up. This leaves behind water sufficiently rich in Ca^{++} and $CO_3^=$ that $CaCO_3$ precipitates around the roots. The carbon in these nodules comes partly from atmospheric CO_2 and partly from respiration CO_2. As these two components have widely different $\delta^{13}C$ values, the $CaCO_3$ records their proportions. However, account must be taken of the isotope fractionation between CO_2 and $CO_3^=$. As this fractionation is temperature dependent (~0.1‰ per °C), it adds to the uncertainty of CO_2 reconstructions. The reason is that dry land soils can have summer temperatures as much as 10 or so °C higher than the overlying air.

respiration CO_2. However, if at some time in the past, the atmospheric pCO_2 was several thousand μatm, then the $\delta^{13}C$ of soil gas would have been correspondingly 'heavier'.

The problem with this proxy is that, for any given $\delta^{13}C$ measurement on paleo-soil $CaCO_3$, the reconstructed atmospheric CO_2 content depends strongly on the 'guesses' as to what the respiration CO_2 partial pressure was at the time the soil carbonate formed. I say, 'guesses' because the soil CO_2 pressure could have been anywhere in the range from 2000 to 9000 μatm. An additional complication is that the isotope fractionation between CO_2 and $CaCO_3$ depends on soil temperature. As soil temperature in dry lands where soil $CaCO_3$ forms can be as much as 10°C or so warmer than the overlying air, the magnitude of this excess must also be guessed at. Until comprehensive studies have been made of factors influencing respiration CO_2 and temperatures in contemporary dry land soils where $CaCO_3$ nodules occur, the results of CO_2 reconstructions made in this way remain highly questionable (see Chapter 6). At the very best, they provide atmospheric CO_2 estimates no better than plus or minus one thousand μatm. But even so, if the soil $CaCO_3$ has as a $\delta^{13}C$ lower than today's values, it does tell that the atmosphere's CO_2 was higher at that time.

Despite its major shortcomings, this proxy is currently one of two that has been used to reconstruct atmospheric CO_2 content for times greater than 38 million years. Hence it is important to conduct research designed to narrow the wide range of uncertainty currently associated with converting ^{13}C to ^{12}C ratios in soil $CaCO_3$ into past atmospheric CO_2 contents. The other is the stomatal resistance method based on stomatal size and density plus bulk leaf ^{13}C.

An Atmospheric O_2 Proxy?

Has the atmosphere's O_2 remained the same? Scientists at the University of Alberta suggest that 50 million years ago it was about 30 percent lower than now (i.e., 0.15 atm instead of today's 0.21 atm). They base this estimate on ^{13}C to ^{12}C ratios measured in amber-like resins produced by trees (Fig. 3-6). They chose amber because: 1) it is produced only by C-3 plants, 2) it constitutes a well-preserved archive, and 3) amber as old as 200 million years

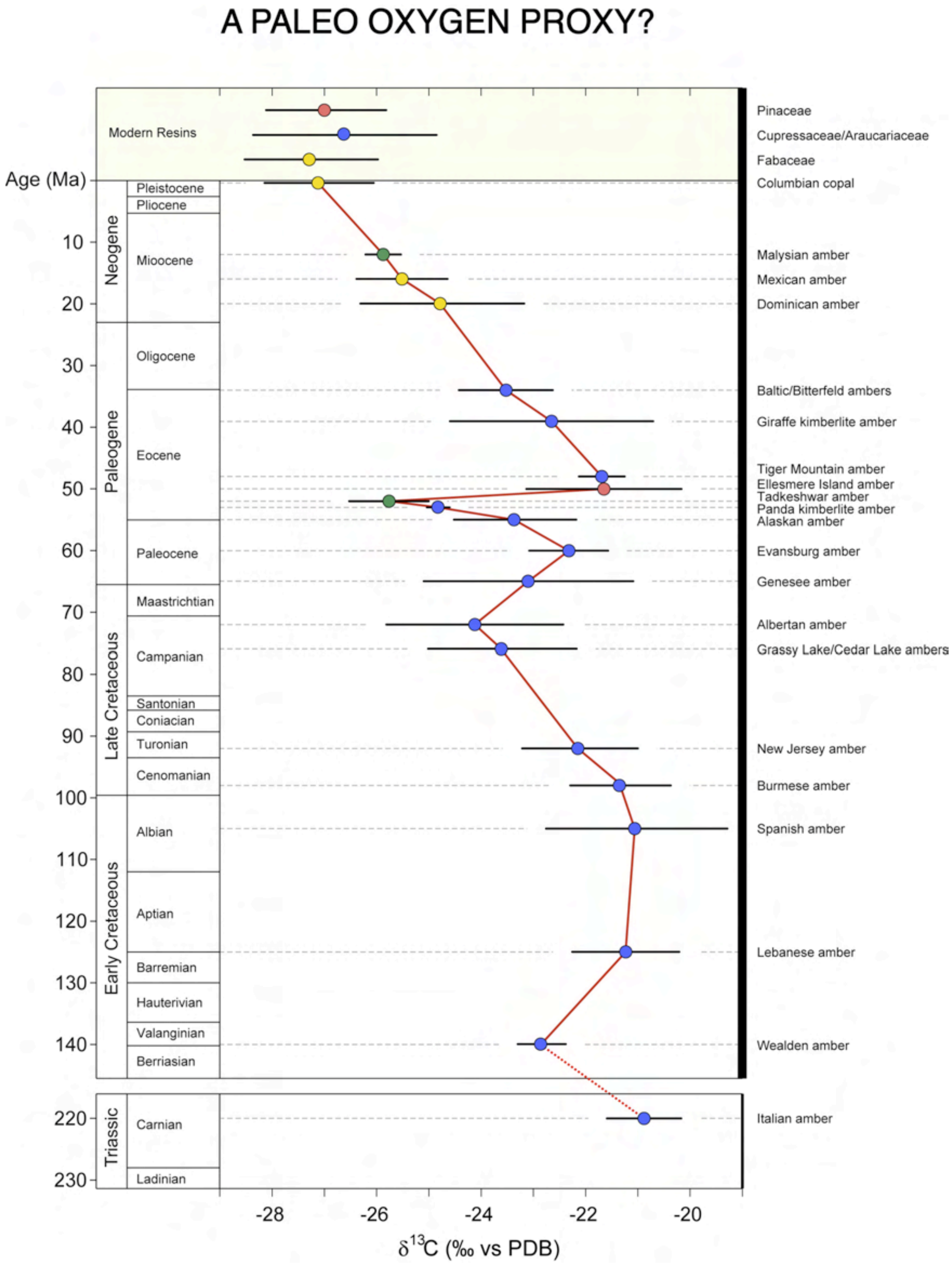


Figure 3-6. The carbon isotopic record as contained in amber (Tappert et al., 2013). The ranges represent the spread for samples of the same age.

exists. What they found is that for the most part ancient resins are less deficient in ^{13}C than contemporary resins. This was counter to expectation. The reason is that at these times the CO_2 content of the atmosphere is thought to have been higher than now. If so, the resins should have been more deficient in ^{13}C rather than less deficient than they are now.

In order to explain this, Tappert et al. call on the reaction of O_2 with the photosynthetic enzyme rubisco. It is well known that rubisco not only reacts with CO_2 to form organic matter but it also reacts with O_2 to destroy organic matter. The idea is that the CO_2 released by this oxidation of organic matter is depleted in ^{13}C relative to air. For example, if 10 percent of the CO_2 utilized for photosynthesis were recycled, the $\delta^{13}C$ of the photosynthate would be about two per mil lower than that in absence of recycled CO_2. So, were O_2 lower in the past, so also would be the contribution of recycled CO_2.

Berner et al. report on two experiments designed to determine the dependence of the use of recycled CO_2 on the O_2 to CO_2 ratio of air. They compared the $\delta^{13}C$ for an angiosperm and for a cycad grown in air with 35 percent and 21 percent O_2 (and with a single CO_2 content of 330 μatm). For the angiosperm, they found that with higher O_2, the $\delta^{13}C$ dropped by 1.4 ± 1.0 per mil and for the cycad by 3.2 ± 1.0 per mil. Although these experiments appear to confirm that recycled CO_2 derived from photo-oxidation does reduce the ^{13}C to ^{12}C ratio in plant material, more such experiments must be conducted in order to pin down the relationship between the reduction in $\delta^{13}C$ and the O_2 to CO_2 ratio. Berry et al. (1972) conducted similar experiments. They held CO_2 constant (at 385 μatm) and compared the $\delta^{13}C$s for growth of a C-3 plant in 21 percent O_2 with that at 4 percent O_2. They found that growth at low O_2 raised the $\delta^{13}C$ only by 2.1‰.

These laboratory experiments are at odds with the Tappert et al. conjecture that the amber carbon isotope record serves as an atmospheric O_2 proxy. They conclude that a 30 percent drop in O_2 caused a 4 per mil increase in plant $\delta^{13}C$. Yet the lab experiments show that a five-fold drop in O_2 produces only a 2 per mil shift. Further, if CO_2 were higher than now, 50 million years ago the situation would be even worse. The reason is that the O_2 drop would have to compensate for the CO_2 impact on $\delta^{13}C$ as well. To me, the amber record is an enigma.

The Sulfur Isotope Proxy

An excellent sulfur isotope record is kept in marine barite (Fig. 3-7). As does the ^{13}C to ^{12}C record in limestone, the ^{34}S to ^{32}S record in barite records the partitioning of sulfur between its reduced form ($S^{=}$) and its oxidized form ($SO_4^{=}$). In order to calculate the split between deposition as FeS and deposition as $CaSO_4$ in marine sediments, the δ^{34}S of the sulfur being added to the ocean-atmospheric reservoir and the extent of fractionation during bacterial conversion of sulfate to sulfide must be known. The conventional choices are +10 per mil for the S added to the ocean and -40 per mil for the fractionation when sulfur is converted from its oxidized to its reduced form. If these figures are accepted, then the current $\delta\, ^{34}$S (i.e., +22) value for ocean sulfur corresponds to 75 percent burial as $CaSO_4$ and 25 percent burial as FeS. But because the isotope separation during sulfur reduction is far more variable than that for carbon reduction, ^{34}S-based reconstructions are subject to much larger uncertainties than ^{13}C-based reconstructions.

Centered at about 50 million years ago, the δ^{34}S for marine SO_4 underwent an upward shift of 4 per mil (from 18 to 22 per mil). This step-wise increase occurred at the end of an earlier long interval of near constancy. It occurred at the time the northward drifting Indian subcontinent collided with Asia.

As suitable barite samples are found only in open ocean sediments, the record is limited to the last 120 million years. However, there is a record extending much further back in time. It comes from evaporites. Way back in 1966, UCLA's Holser and Kaplan measured the sulfur isotope ratios in a host of such samples (Fig. 3-8). However, unlike Paytan's barite record, it is spotty in time. As evaporites form only sporadically, Holser and Kaplan could not produce a continuous record. There were times, such as the Triassic, where none were available to them. Also, since 1966 when their paper was published, there have been major adjustments in the absolute time scale. A graduate student working in Jess Adkins Caltech laboratory has recently reproduced the Payton barite based on the trace sulfur contained in foraminifera shells.

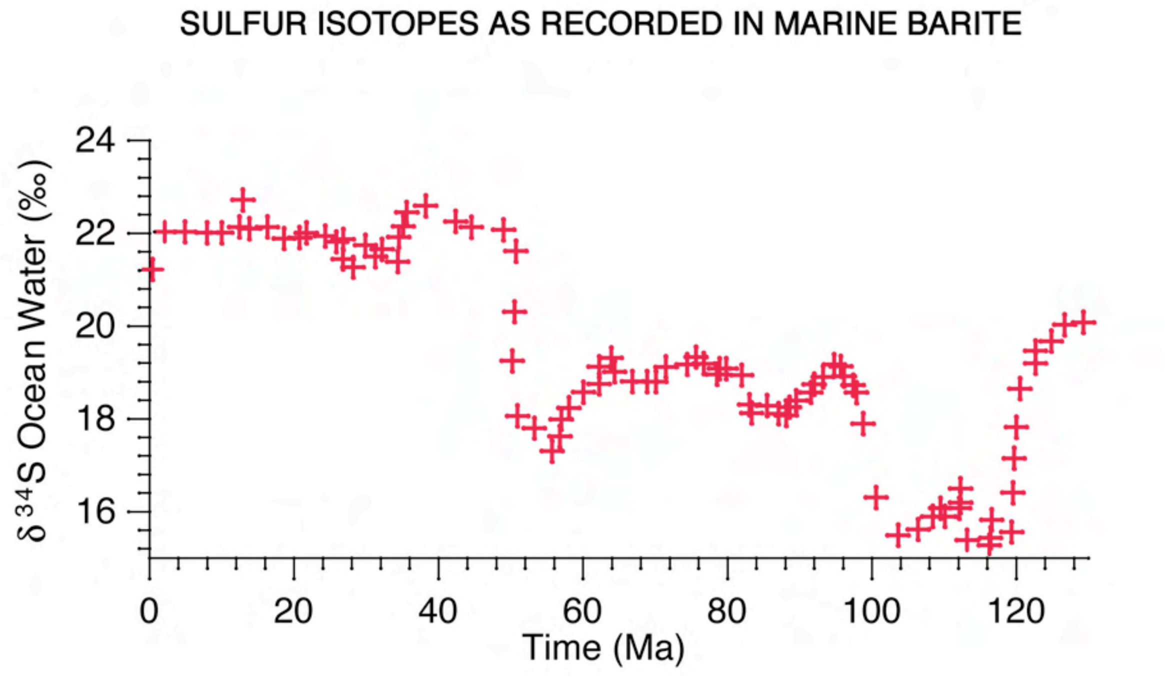


Figure 3-7. The isotopic composition of sulfate as recorded in marine barite (Paytan et al., 2004).

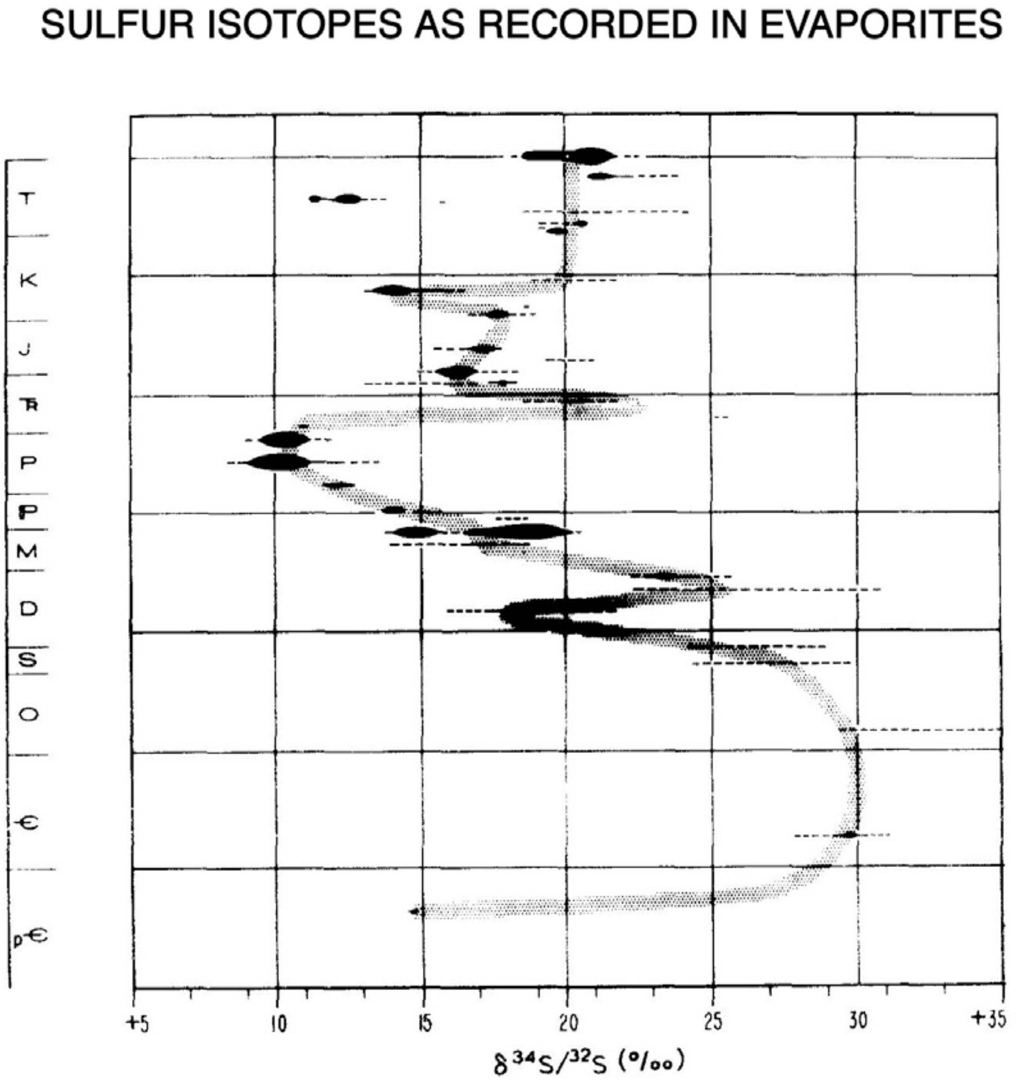


Figure 3-8. The isotopic composition of marine SO_4 as recorded in evaporites (Holser and Kaplan, 1966). As the geologic time scale has undergone major revisions since this paper was published, the absolute age scale has been deleted.

Boron-based Carbonate Ion Proxy

While a graduate student working with Cambridge University's Harry Elderfield, Jimin Yu developed a surprisingly reliable method to determine glacial to interglacial changes in deep ocean carbonate ion concentration. It involves the B to Ca ratio in the calcite formed by the benthic foraminifera, Cibicides. By measuring the boron to calcium ratio from Cibicides core-tops from a wide range of depths and locations, he found a very tight correlation with the degree of calcite supersaturation (see Fig. 3-9). Over the time interval of glacial cycles, it is safe to assume that neither the calcium nor the boron content of seawater changed significantly. Yu demonstrated that the dependence is on the degree of calcite saturation rather than the carbonate ion concentration itself. In particular, this was demonstrated by core-top Cibicides from various depths and locations in the in the deep ocean. Even though the in situ carbonate ion concentration is nearly uniform with depth, he found that the deeper the sediment, the lower the B to Ca ratio in the core-top shells. But, when plotted against the degree of saturation, these depth differences disappeared. Even though his method does not yield absolute carbonate ion concentrations, it does yield changes in the concentrations of $CO_3^=$ at any given locale. For example, the difference in the B to Ca ratio between shells of peak glacial age and of late Holocene age from the same sediment core tells us the change in carbonate ion. When this difference is added or subtracted from directly measured concentrations in today's ocean, it yields the peak glacial concentration. This works because the pressure at a given coring site changes only because of the changes in sea level. However these pressure changes are sufficiently small that they needn't be considered.

Although great for tracking the deep sea $CO_3^=$ concentration through the ice ages, going back further in time raises difficulties. One reason is that the dependence of B to Ca on the extent of the degree of calcite undersaturation differs widely from one species of benthic foraminifera to another. Although Cibicides ancestors appeared early in the Cenozoic, its form has evolved. There is no way to know whether or not, as they evolved, the

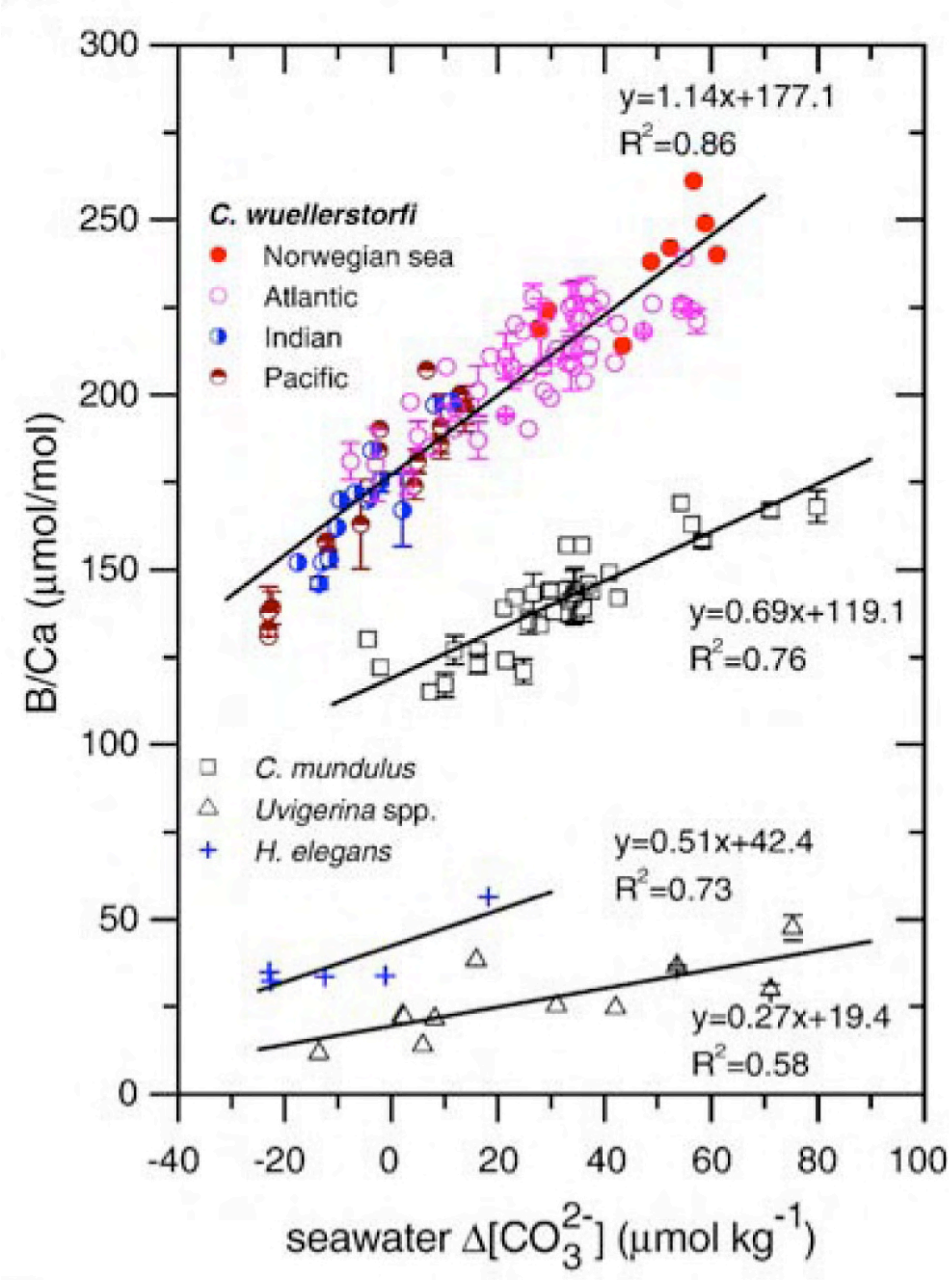


Figure 3-9. Boron to calcium ratio in Holocene-age benthic foraminifera shells as a function of the extent of $CaCO_3$ super-saturation as determined by Yu and Elderfield. As can be seen, this relationship is highly species dependent. However, the percentage change in B to Ca ratio with increasing $\Delta CO_3^{=}$ is about the same for each species.

slope of the correlation between its B to Ca ratio and the extent of calcite undersaturation also evolved. Further, as we shall see, the calcium content of seawater appears to have decreased by a factor of two over the last 50 million years. The boron content may have changed as well. It is interesting to note that despite the large benthic species to benthic species differences in boron content, the percentage change in boron content with changes in supersaturation are similar.

The Compensation Depth Proxy

An alternate approach to reconstructing the carbonate ion concentration in the deep sea involves reconstructions of the depth of calcite saturation horizon. As already discussed, the transition from carbonate-rich ooze to red clay marks the depth of this horizon. Hence, deep sea sediments potentially contain a record of the product of the concentrations of Ca^{++} and $CO_3^{=}$ ion. As a consequence of the pressure dependence of the solubility product, for each kilometer the horizon moves up or down, the saturation product rises by about 15 percent. Hence, if the calcium content of ocean water could be independently reconstructed, this observation could be used to constrain the carbonate ion concentration. I say potentially because several complications must be dealt with.

First of all, the saturation depth itself cannot be defined to better than several tenths of a kilometer. The reason is that the change in $CaCO_3$ content of sediments exposed to dissolution is highly nonlinear (Fig. 3-10). The greater the extent of dissolution, the more rapidly the content drops. Because of this, the common practice is to use the depth where the $CaCO_3$ content of the sediment drops to 20 percent as a stand-in for the depth of the saturation horizon. It is referred to as the compensation depth. Then, if the offset between the saturation depth and the compensation depth were the same everywhere and at all times, the shifts in the depth of saturation horizon would reflect those for the compensation horizon itself. However, as the depth offset depends on the ratio of the rate of accumulation of $CaCO_3$ to that of non $CaCO_3$ (i.e., clay, ash, opal…), such reconstructions have an uncertainty of several hundred meters.

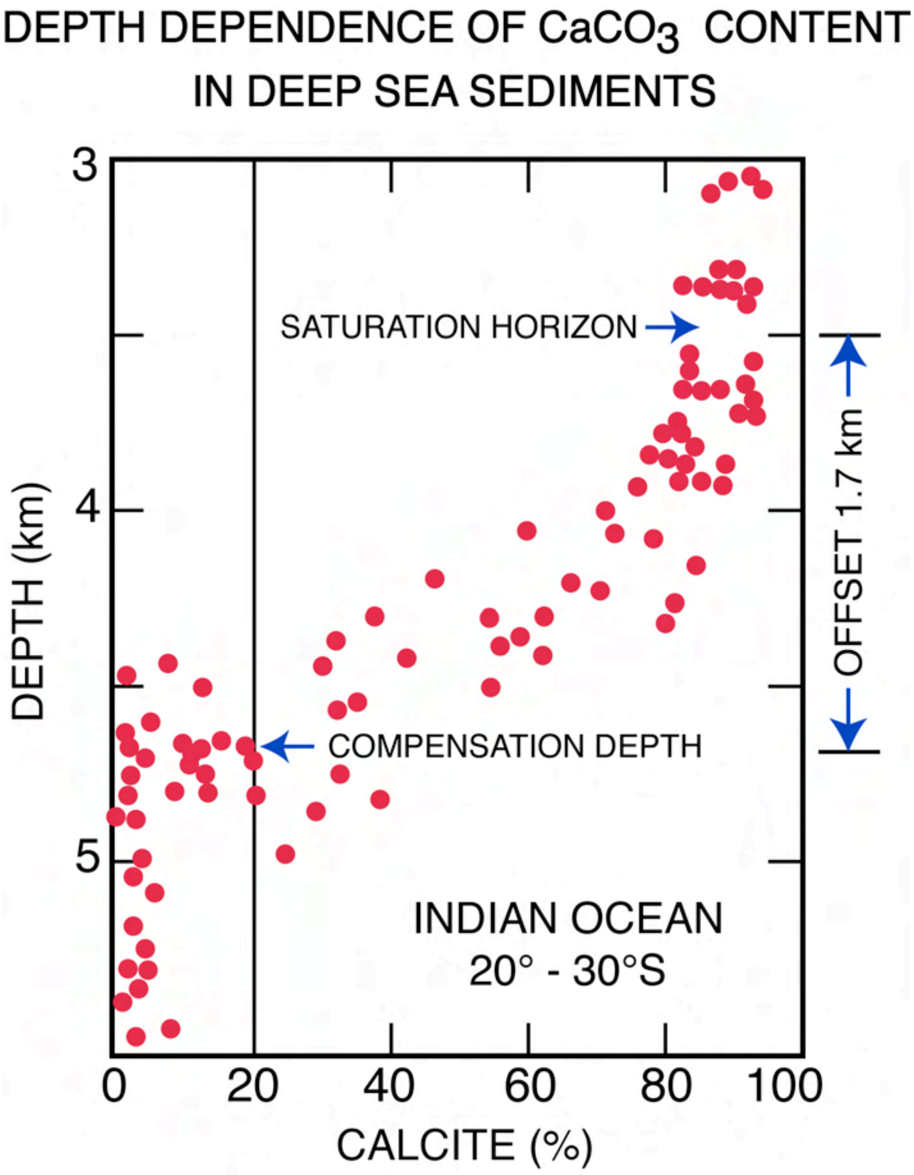


Figure 3-10. Example of the change with water depth of the $CaCO_3$ content of marine sediments. As can be seen, the decline in $CaCO_3$ content becomes clear at about 4.0 km and is completed by a depth of about 4.7 km. The scatter reflects differences in the accumulation rate ratio of $CaCO_3$ to that of non $CaCO_3$. The calcite saturation horizon is close to 3.5 km and the compensation depth at about 4.7 km. Within this transition zone, the rate of $CaCO_3$ dissolution is less than that of the $CaCO_3$ rain to the sea floor. Hence a portion of the $CaCO_3$ survives.

A second correction involves the deepening of the sea floor with time. At the ridge crest the ocean crust has a depth averaging 2.5 km. At the subduction zone, it has a depth of about 5.5 km. This subsidence is the result of the cooling of the lithosphere as the crust moves away from the hot ridge crest. As the rate of cooling decreases with the square root of time, the extent of crustal shrinkage can be reconstructed based on the time of the ooze to clay transition (Fig. 3-11).

Another consideration is that the saturation product of Ca^{++} and $CO_3^{=}$ ions depends not only on pressure but also on temperature. During the last 50 million years, the deep ocean has cooled by about 10°C. Fortunately, the ^{18}O record kept by benthic foraminifera constrains this temperature correction.

Finally, the activity coefficient of carbonate ion in sea water differs widely from that in fresh water. In today's ocean complexing of $CO_3^{=}$ with the cations Na^{+}, Mg^{++} and Ca^{++} reduces its activity by tenfold. As we will see, substantial changes in the composition of sea salt have occurred. For example, over the last 50 million years Mg^{++} has gone up and Ca^{++} has gone down.

A final consideration is that the depth of the saturation horizon differs with location in the ocean. Today it is about one kilometer deeper in the Atlantic than it is in the Pacific. The reason is that the $CO_3^{=}$ concentration in the deep Atlantic averages 110 μmole per liter while that in the deep Pacific is closer to 90 μmole per liter. This difference reflects the twofold higher phosphate content of the deep Pacific water (and its companion respiration CO_2). As there is every reason to suspect that such inter-ocean differences existed in the past, these reconstructions should be conducted in each major ocean basin.

Magnesium to Calcium Ratio

A variety of evidence tells us that over the last 100 million years the Mg to Ca ratio in sea water has undergone a several fold increase. But reconstructing the time history of this change has posed a particularly large challenge. Four archives place constraints on the magnitude of this increase. They are: 1) the composition of halite-hosted fluid inclusions; 2) the Mg content of

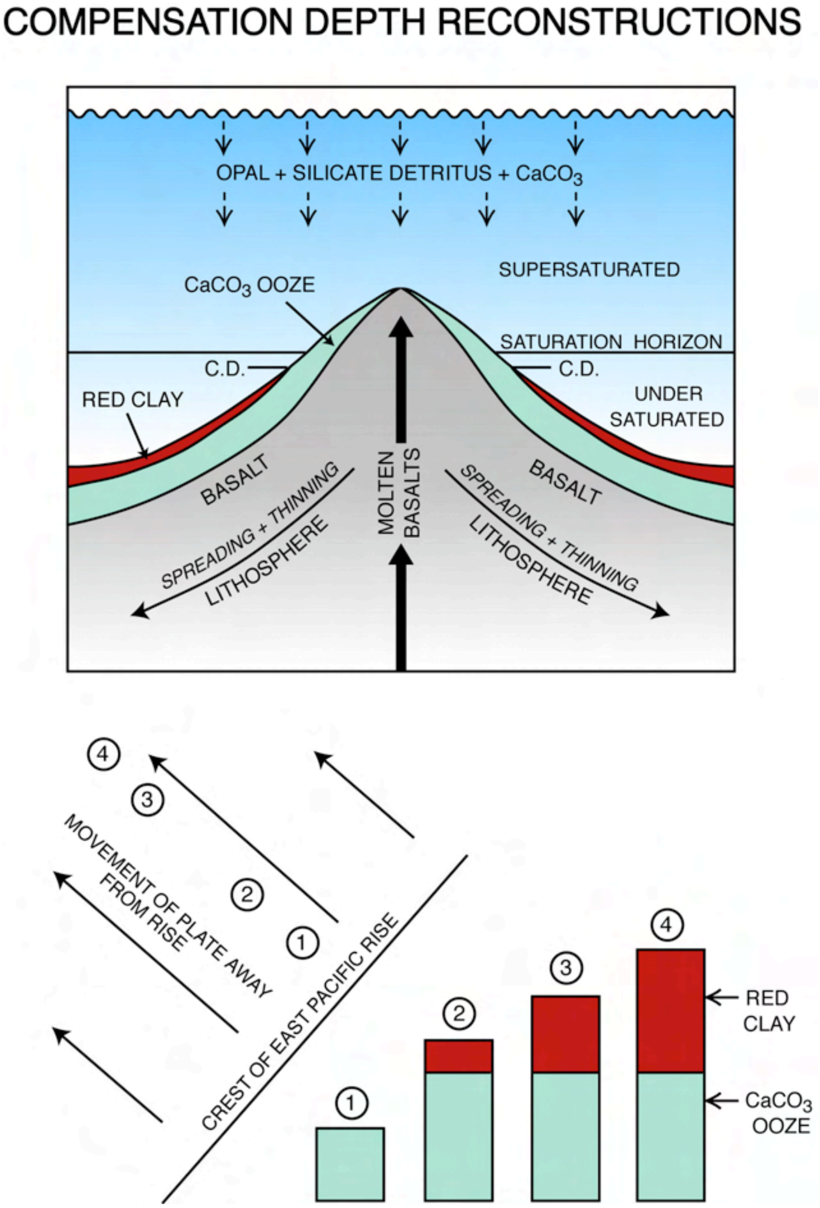

COMPENSATION DEPTH RECONSTRUCTIONS

Figure 3-11. Basalts form at mid-ocean spreading centers. During their long trip across the sea floor away from the hot ridge crest, the lithosphere slowly cools and as a result shrinks in thickness. This results in a progressive deepening of the sea floor. At some point, the sediment water interface drops below the saturation horizon for calcite and the $CaCO_3$ begins to dissolve. As sinking proceeds, an ever greater percent of the $CaCO_3$ dissolves until only the opal and clay remain. By backtracking the subsidence to the time of $CaCO_3$ ooze-red-clay transition, the compensation depth (i. e., C. D.) at the time of the transition can be reconstructed.

the calcite precipitated in veins in sea-floor basalts; 3) the Mg content of planktonic foraminifer shells; 4) the Mg content of aragonitic corals. Even though each of these archives has its drawbacks, taken together, they present a consistent if not highly accurate story. Over the last 50 million years the Mg appears to have increased by about a factor of about two and Ca has decreased by about a factor of two.

The most important of these archives is that kept by fluid inclusions in marine halite (Figs. 3-12 and 3-13). The most extensive studies of these inclusions has been carried out in Tim Lowenstein's laboratory in SUNY Binghamton. Four episodes of salt deposition have proven suitable for this purpose. Each was created by the evaporative enrichment of sea salt in a topographically isolated arm of the ocean. The most recent of these halites formed as the result of the isolation of the Mediterranean Sea five million years ago. The oldest was deposited during the creation of the Atlantic about 110 million years ago. The other two formed in Europe: one 12 million years ago and the other 34 million years ago.

Although these inclusions serve as a pristine archive, they suffer from a serious limitation. It has to do with the formation of gypsum (Ca SO_4). Long before the salinity in an isolated basin reaches the point where halite begins to precipitate, either its Ca or its SO_4 is totally depleted as the result of the deposition of gypsum. In the case of the 110 million-year-old halite, SO_4 was the first to be depleted. In the three younger halites, calcium was the first to be depleted. Because of this, in the three younger halites, nothing can be said about the concentration of Ca and only a lower limit can be placed on the amount of sulfate. For the older one, the opposite is true. But taken together, the inclusions tell us that 110 million years ago the amount of calcium in the ocean exceeded the amount of sulfate and that for the last 40 million years sulfate has exceeded calcium.

A basic complication is that the concentrations of all the ions in the fluid inclusions in halite are highly enriched by evaporation and hence are far greater than they were in the parent seawater. To get around this obstacle, the assumption is made that the potassium content of seawater has not changed with time. The content of potassium can then be used to

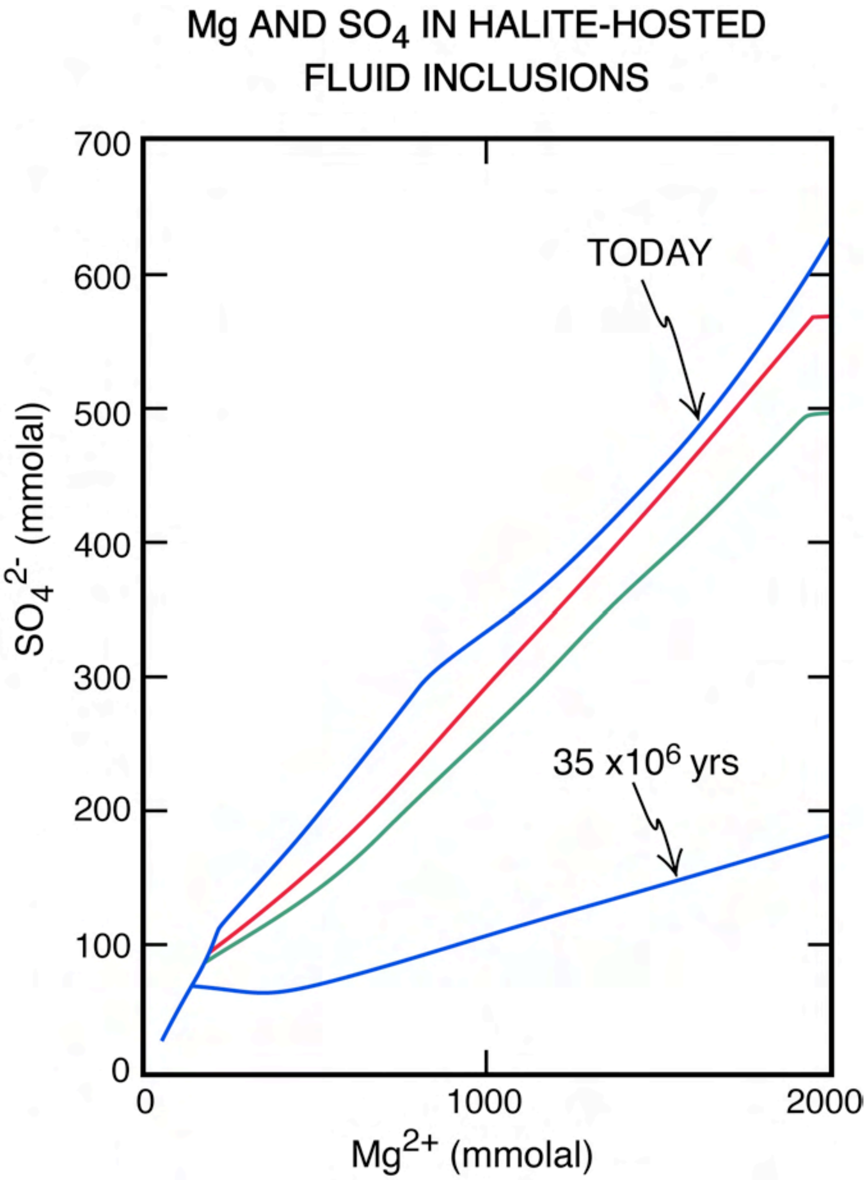
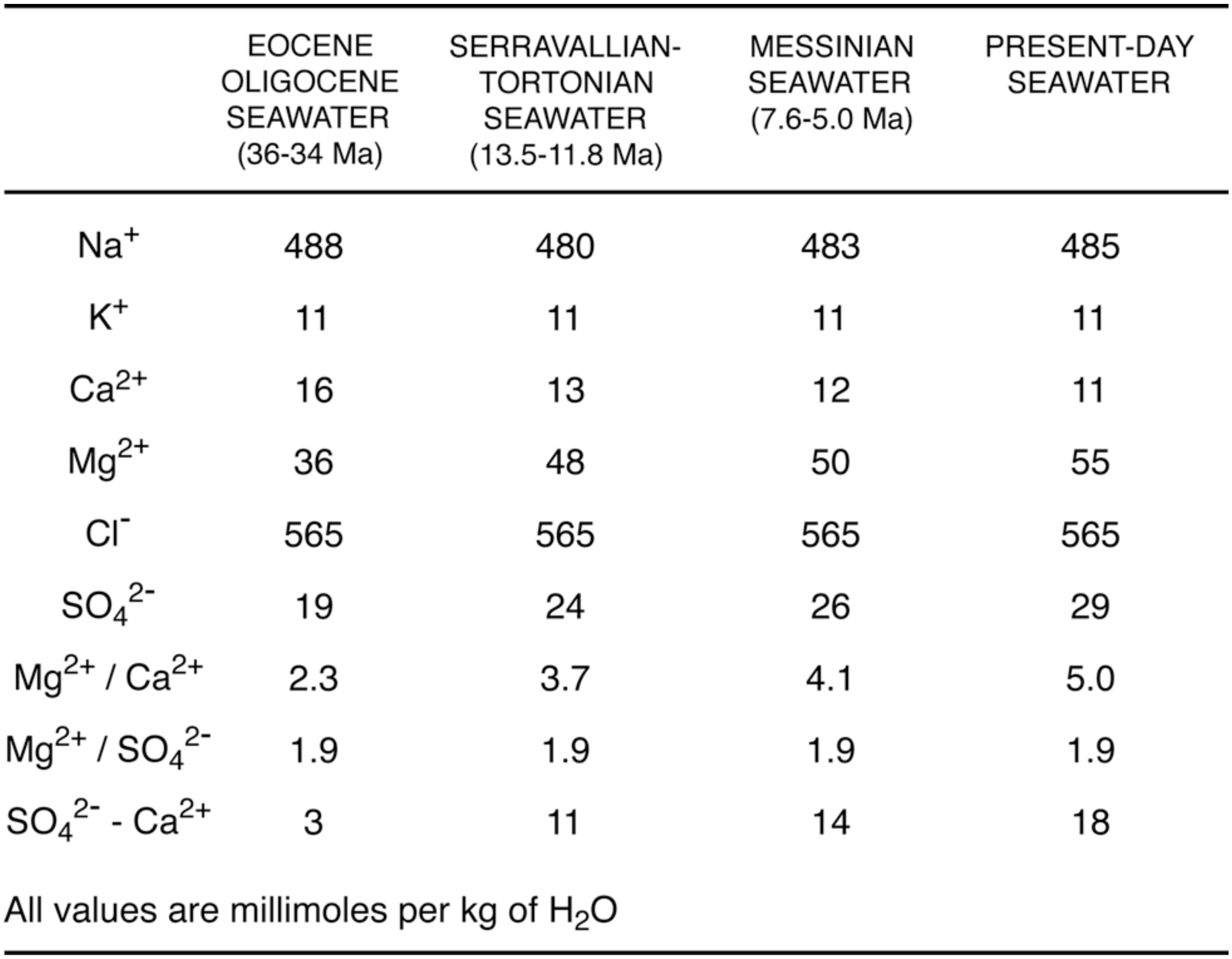


Figure 3-12. Comparison of the up section trends of the Mg^{++} to $SO_4^{=}$ ratio in halite-hosted fluid inclusions with that obtained by evaporative concentration of today's seawater. Halite - hosted inclusions of three ages are shown. The red line is for 6 million-year-old halites, the green line for 12 million-year-old halites and the blue line for 35 million-year-old halites. The much lower SO_4 concentration in the 35 million-year-old inclusions likely reflects a larger loss to the formation of gypsum, presumably because there was more calcium in seawater at that time. To understand this, keep in mind that the $SO_4^{=}$ in the inclusions is that remaining after all the Ca^{++} had been precipitated as gypsum (Brennan et al., 2013).



	EOCENE OLIGOCENE SEAWATER (36-34 Ma)	SERRAVALLIAN-TORTONIAN SEAWATER (13.5-11.8 Ma)	MESSINIAN SEAWATER (7.6-5.0 Ma)	PRESENT-DAY SEAWATER
Na^+	488	480	483	485
K^+	11	11	11	11
Ca^{2+}	16	13	12	11
Mg^{2+}	36	48	50	55
Cl^-	565	565	565	565
SO_4^{2-}	19	24	26	29
Mg^{2+} / Ca^{2+}	2.3	3.7	4.1	5.0
Mg^{2+} / SO_4^{2-}	1.9	1.9	1.9	1.9
$SO_4^{2-} - Ca^{2+}$	3	11	14	18

All values are millimoles per kg of H_2O

Figure 3-13. Summary of estimates of the evolution of the composition of sea salt over the past 35 million years based on measurements of the chemical composition of halite-hosted fluid inclusions (Brennan et al., 2013). Critical to this reconstruction is the assumptions that the concentration of potassium and the ratio of Mg^{++} to $SO4^{=}$ has not changed. As no calcium is present in the inclusions, the assumption is also made that the product of Ca and $SO4^{=}$ concentrations has remained unchanged. A third assumption is that the Cl^- content of seawater has not changed. As none of these assumptions need be correct, these estimates must be taken with 'a grain of salt'!

gauge the extent of evaporative enrichment. If this assumption is valid, then the Mg to K ratios in the fluid inclusions allows the change in magnesium content of seawater to be estimated. But the answer is only as good as the assumption that the potassium content of seawater has not changed. Cross checks based on bromine lend support to the constancy of potassium.

One way to evaluate the integrity of the halite archive is to do up-section sequences. If such a series represents the accumulation of halite from a single isolation episode, then the concentrations of all the ions should show a steady up-section increase and, of course the ratio of Mg to K should remain unchanged.

If Mg^{++} has increased with time, it might be expected that in order to maintain charge balance, the concentration of Ca^{++} would have correspondingly decreased. But this requires that the concentrations of the other ions remained unchanged and, in particular, that of $SO_4^{=}$. As already mentioned, the observation that at some time between 110 and 35 million years the ratio of Ca^{++} to $SO_4^{=}$ dropped below unity is consistent with a decrease in Ca^{++}. But it could also reflect an increase in $SO_4^{=}$.

A qualitative observation lends support to an increase in the Mg^{++} to Ca^{++} ratio. Prior to about 50 million years ago, the $CaCO_3$ in reefs was largely calcitic. Since then it has been largely aragonitic. Laboratory experiments suggest that if the Mg to Ca is much lower than today's, the precipitation of calcite is favored.

The second approach is to measure the Mg content of calcite precipitated in the cracks present in ridge crest basalts (Fig. 3-14). It is assumed that these calcites formed shortly after the host basalt formed. Strontium isotope measurements on these calcites confirm this assumption. But, as in the case of halite inclusions, there are problems associated with the interpretation of these results. First, it must be assumed that the coefficient relating the Mg to Ca ratio in the calcite to that in seawater varies only with water temperature. But it is well known that in low temperature situations growth rate influences the incorporation of trace constituents.

As the youngest of the calcites, i.e., that from the Juan de Fuca Rise off British

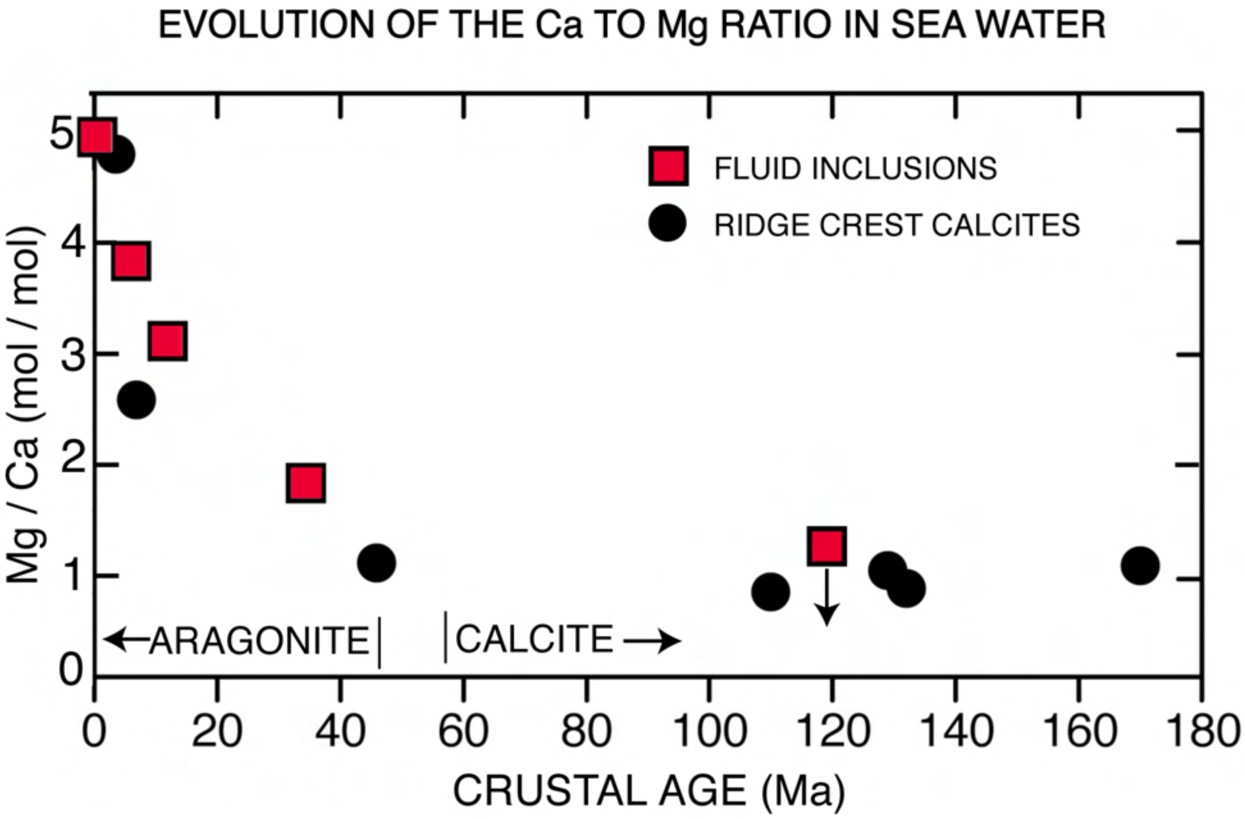


Figure 3-14. Time trend of Mg to Ca ratios in seawater as reconstructed from measurements on halite-hosted fluid inclusions (Brennan et al., 2013) and from those on ridge crest calcites (Coggon et al., 2010). Although both proxies have bothersome uncertainties, they do tell consistent stories. The Mg to Ca ratio in seawater appears to have risen by about a factor of five over the last 180 million years. Most of this rise has occurred during the last 50 million years.

Columbia, is only a million years old, it can be assumed that the Mg to Ca ratio in seawater was close to todays. In this way the needed coefficient relating Mg to Ca ratio in calcite to that in sea salt has been determined. But, as has been shown for the calcite formed by foraminifera, the Mg content increases with temperature. If the young basalts had not cooled to ambient bottom water temperatures, then the calcites would have formed at elevated temperatures. That this is the case has been shown from measurements on the calcite ^{18}O to ^{16}O ratio. In order to minimize the required temperature correction, the results for calcites which formed at temperatures closest to that of deep seawater are given more weight. Although I am dubious regarding the ability to reliably determine the appropriate distribution coefficient, I must admit that the results obtained in this way are broadly consistent with those based on halite inclusions and reef mineralogy (see Fig. 3-14). They suggest that the Mg to Ca ratio in seawater remained low until about 50 million years ago and then underwent a several-fold increase.

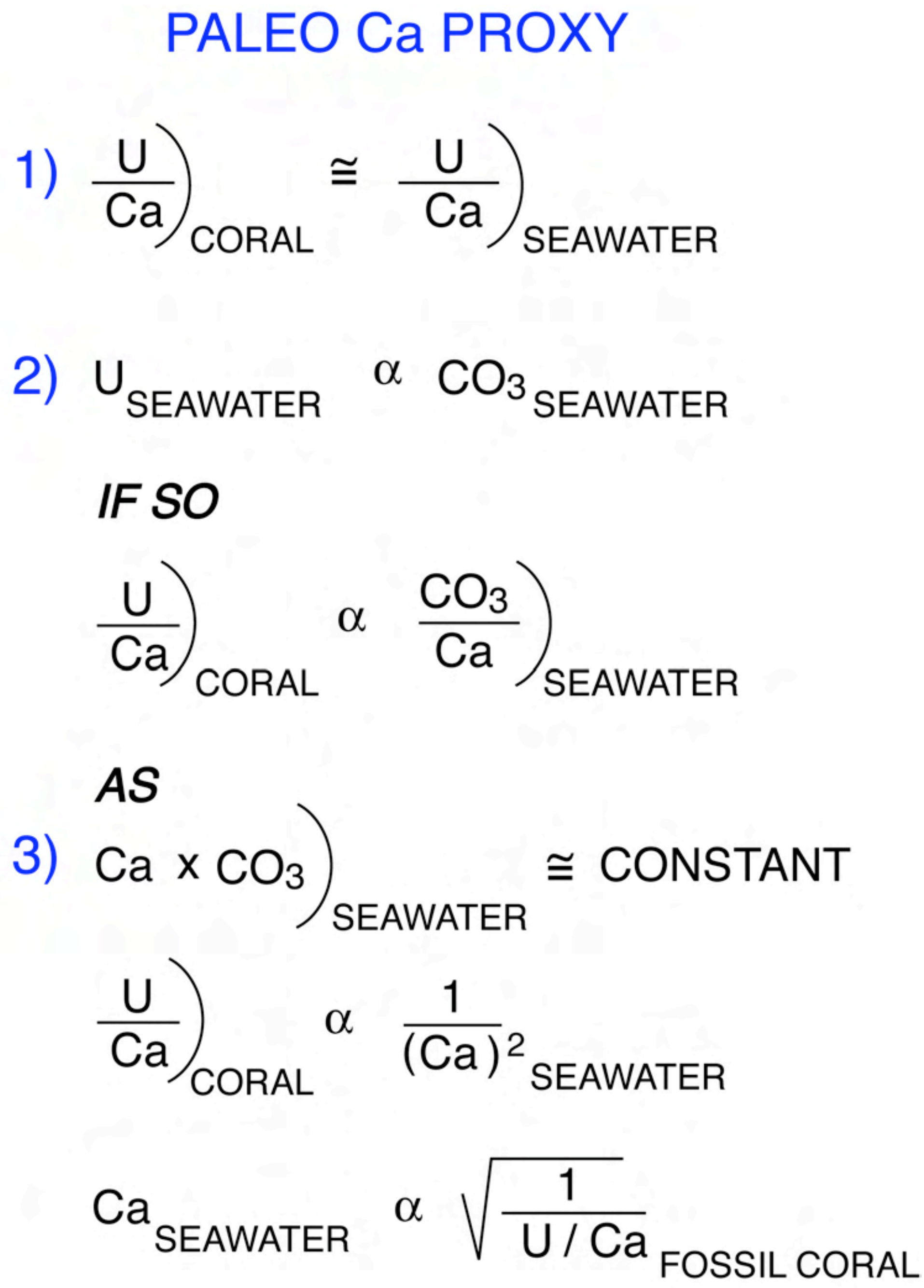
In the same way that ridge crest calcites record Mg, so also do the calcite shells of foraminifera. The Mg content of foraminifer shells has been shown to depend on water temperature. The warmer the water, the more Mg they contain. The difference is that for ridge crest calcites the deposition is inorganic and for foraminifera it is biogenic. Creatures introduce complications. For example, as shown by Howie Spiro at U.C. Davis, the magnesium content of shell material deposited in the dark differs from that deposited in the light. Only by measuring a composite of a number of such shells can the imprint of this light dependence be averaged out.

The fourth approach is to measure the Mg content of well-preserved aragonitic corals. Anne Gothmann did this as part of her PhD thesis research at Princeton. As her results have yet to be published, I don't include them here. But, I can say that they are consistent with those obtained from halite-hosted fluid inclusions and ridge crest calcites.

Many measurements of Mg to Ca ratios have been obtained for planktic foraminifera formed before and following the PETM event. They have Mg to Ca ratios close to those found in Holocene sediments. But as surface ocean temperatures 55 million years ago were likely warmer than today's, when corrected for the temperature difference, the reconstructed Mg to Ca ratio is smaller than today's. How much smaller depends on how much warmer it was.

Early in my career, I proposed that the uranium content of aragonitic corals might be used as a proxy for the Ca^{++} content of seawater. Three assumptions were required (Fig. 3-15). First that the U to Ca ratio in corals is close to that in seawater. Second that the U content of seawater is proportional to its carbonate ion concentration. Third, that the extent of supersaturation of aragonite in tropical surface water has remained constant. Measurements on a host of corals of Holocene age and last glacial age indicate that to within ±15 percent the first assumption is valid. The second assumption was initially shaky as it was originally based solely on the observation that alkaline Mono Lake which has a carbonate ion concentration two orders of magnitude higher than that for seawater also has a two order of magnitude higher uranium content. However, I recently was alerted to a paper by Linhoff et al. (2011) on the chemistry of five closed basin lakes in eastern Mongolia which supports my supposition. Ranging over two orders of magnitude, the U content matched the DIC content (see Fig. 3-16). The third assumption is based on the near constancy of the $CaCO_3$ compensation depth. But as the difference in composition of surface water and that of deep water may have changed, this assumption is open to question. However, as discussed below, the observation that the difference between the $\delta^{13}C$ in coexisting surface-dwelling and bottom-dwelling foraminifera provides some support for this assumption.

The uranium content of several well-preserved Miocene-age corals is less than that for todays (Fig. 3-17). This suggests that the Ca content of seawater was somewhat higher than now. Although consistent with the other archives, until recently this approach has not been pursued. Hence it remains in limbo. However, as the interpretation of each of the other proxies requires questionable assumptions, perhaps the uranium in coral approach should be given a closer look. It is important to get calcium right for, with it, we can use the compensation



PALEO Ca PROXY

1) $$\left.\frac{U}{Ca}\right)_{CORAL} \cong \left.\frac{U}{Ca}\right)_{SEAWATER}$$

2) $$U_{SEAWATER} \;\alpha\; CO_{3\,SEAWATER}$$

IF SO

$$\left.\frac{U}{Ca}\right)_{CORAL} \;\alpha\; \left.\frac{CO_3}{Ca}\right)_{SEAWATER}$$

AS

3) $$\left.Ca \times CO_3\right)_{SEAWATER} \cong \text{CONSTANT}$$

$$\left.\frac{U}{Ca}\right)_{CORAL} \;\alpha\; \frac{1}{(Ca)^2}_{SEAWATER}$$

$$Ca_{SEAWATER} \;\alpha\; \sqrt{\frac{1}{U/Ca}}_{\text{FOSSIL CORAL}}$$

Figure 3-15. Accepting the validity of three assumptions, the U content of well-preserved aragonitic corals serves as a paleo ocean calcium proxy. However, as the assumptions need validation and as diagenesis may have altered the uranium content of the corals, the method remains in limbo. Uranium measurements on well preserved aragonitic corals, made by Princeton's Anne Gotham, suggest that the calcium content of seawater has decreased over the last 50 million years.

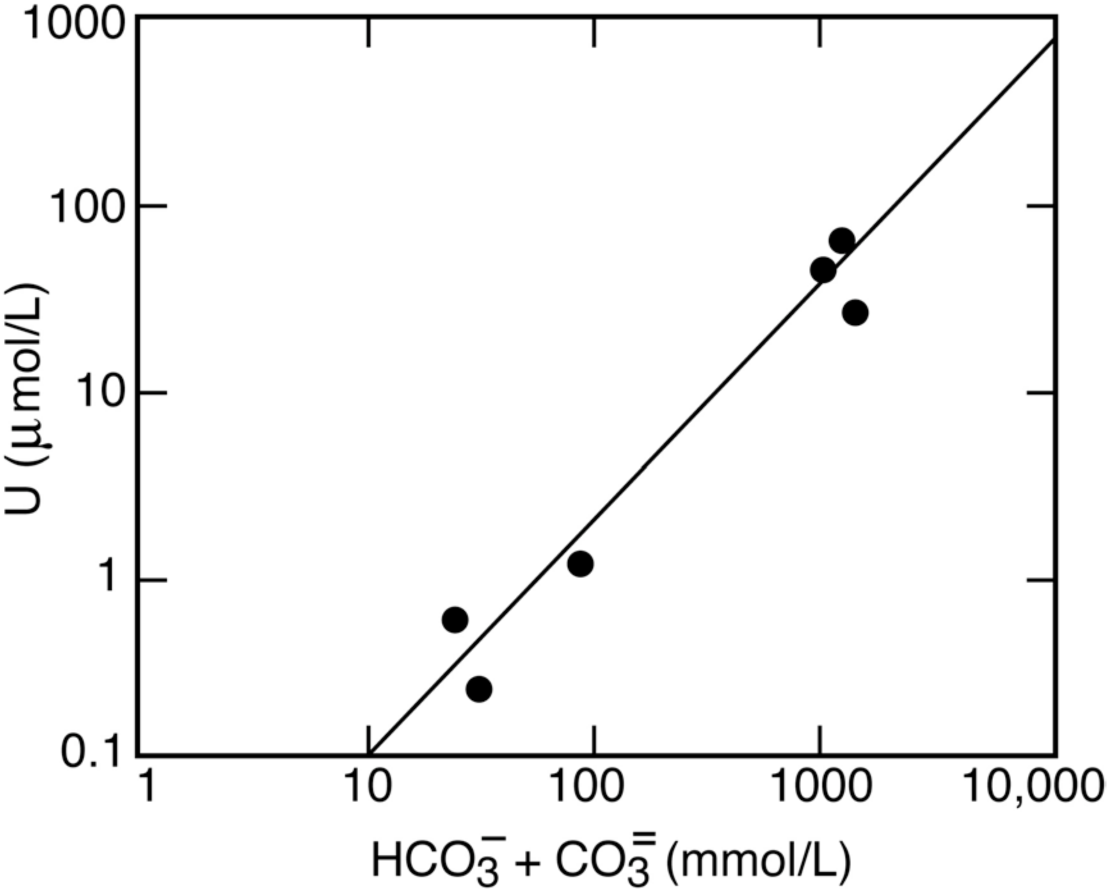


Figure 3-16. The relationship between the uranium content and dissolved inorganic carbon content for five eastern Mongolian closed-basin lakes (Linhoff et al., 2011).

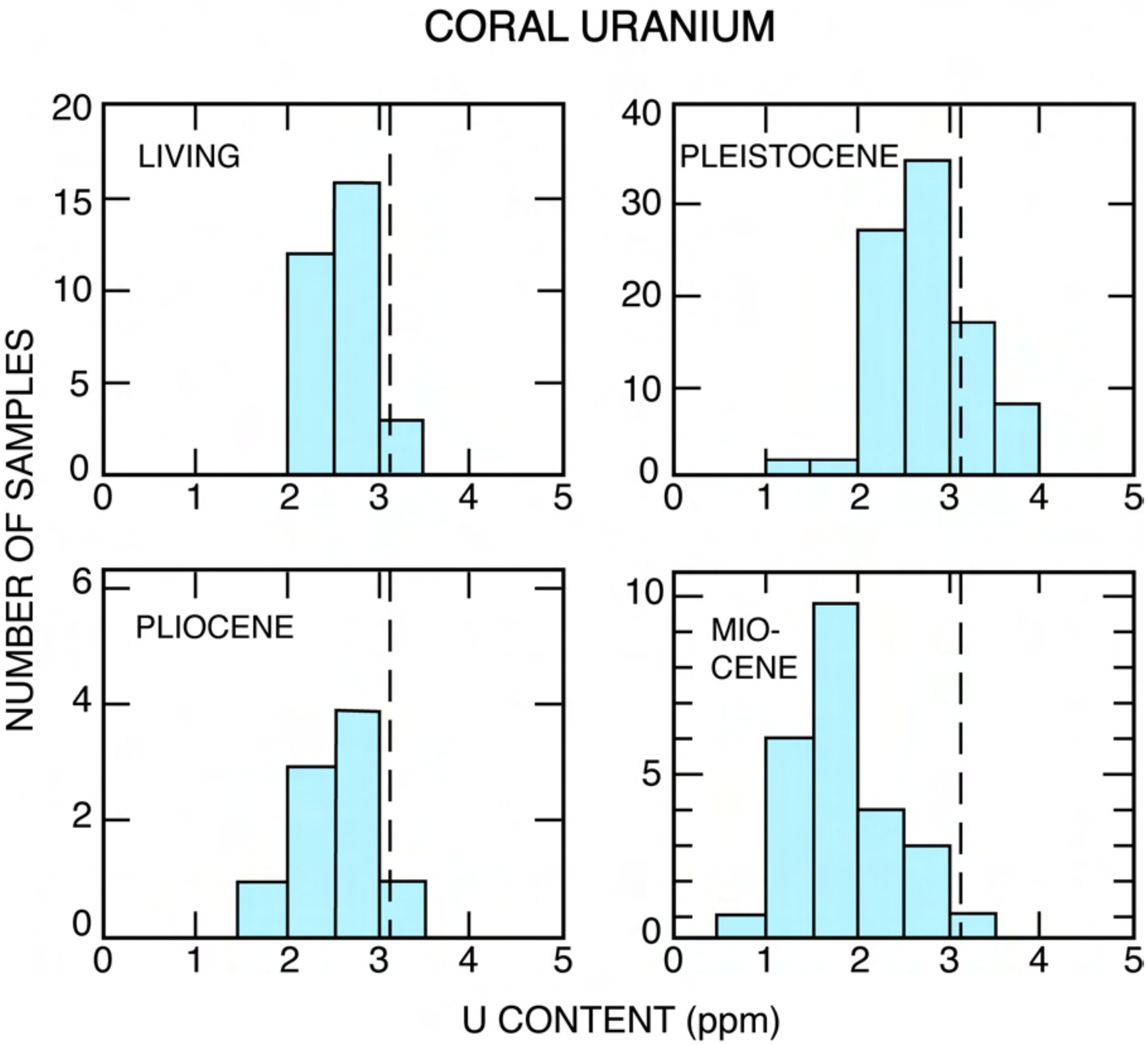


Figure 3-17. Summary of measurements of the uranium content of aragonitic corals in four age classes. Those from the Miocene have a significantly lower uranium content than the others. Taken at face value, this suggests that the calcium concentration in the Miocene ocean was roughly √2 times higher than today's. The vertical dashed line indicates the content expected if the U to Ca ratio in corals were the same as in today's seawater.

depth proxy to establish paleo carbonate ion concentrations for times before the appearance of Cibicides.

A recent breakthrough offers encouragement. Anne Gothmann has measured uranium in her aragonitic corals. She finds that over the last 50 million years, the uranium contents increase. The magnitude of the increase is consistent with that shown in Figure 3-17.

Surface to Deep Composition Difference

We have proxies which allow us to reconstruct the CO_2 content of surface water and proxies which allow us to reconstruct the $CO_3^{=}$ content in deep water. If there were no surface to deep composition difference, taken together, they would allow us to calculate the bicarbonate, carbonate alkalinity and total dissolved-inorganic carbon in past oceans. But today there is a sizable difference in the compositions of these two reservoirs. The production of organic tissue in surface water depletes the dissolved inorganic carbon content of surface water. In so doing it also lowers its CO_2 content and raises its $CO_3^{=}$ content. The production of $CaCO_3$ by some of these organisms reduces the alkalinity of surface water relative to that in deep water. In so doing it partially offsets the differences created by the soft tissue formation.

We do have a proxy for the strength of the soft tissue cycle. It is the ^{13}C to ^{12}C ratio difference between surface and deep water as recorded by coexisting planktic and benthic foraminifer shells (see Fig. 3-18). It depends on three things: 1) the C to P ratio in soft tissue, 2) the carbon isotope fractionation between seawater DIC and soft tissue, and 3) the ΣCO_2 to P ratio in average ocean water. The first of these is assumed to have remained much the same through time. The second is related to the CO_2 content of the water (see above). Knowing these two, the third can be obtained from the difference between the $\delta^{13}C$ in planktic and benthic foraminifera. Based on the records in hand, there has been little change in this difference over the last 60 million years. The $\Delta\delta^{13}C$ between planktic and benthic foraminifer shells has remained close to 1.8 per mil. This suggests that the deep ocean ratio of ΣCO_2 to PO_4 concentration has remained close to 1000.

$PO_4 / \Sigma CO_2$ PROXY

TODAY

$$\Delta\,[PO_4] = 1.8\,\mu mol/kg \begin{cases} [PO_4]_{\text{WARM SURFACE}} = 0.2\,\mu mol/kg \\ [PO_4]_{\text{MEAN DEEP}} = 2.0\,\mu mol/kg \end{cases}$$

$$\Delta\,\delta^{13}C = 1.8\,‰ \begin{cases} \delta^{13}C_{\text{WARM SURFACE}} = 2.0\,‰ \\ \delta^{13}C_{\text{MEAN DEEP}} = 0.2\,‰ \end{cases}$$

$$\Delta\,\delta^{13}C = \Delta\,\delta^{13}C_{\text{PHOTOSYN.}} \times \left.\frac{C}{P}\right)_{\text{ORG.}} \times \frac{\Delta[PO_4]_{\text{MEAN OCEAN}}}{[\Sigma CO_2]_{\text{MEAN OCEAN}}}$$

$$= 18 \times 125 \times \frac{1.8}{2250}$$

$$= 1.8\,‰$$

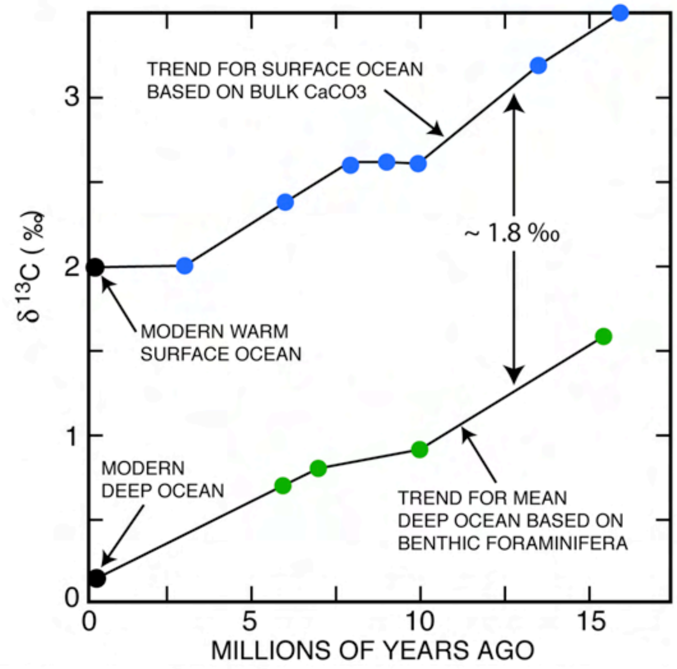


Figure 3-18. The $\Delta\delta^{13}C$ coexisting between planktonic $CaCO_3$ and benthic foraminifera shells serves as a proxy for the ratio of PO_4 to ΣCO_2 in the ocean. It has remained close to 1.8 per mil throughout the last 15 million years. The decline in $\delta^{13}C$ during the last 15 million years is, at least in part, the result of the widespread appearance of C4 grasslands.

However, it is the PO_4 content itself we are after rather than its ratio to ΣCO_2, for PO_4 sets an upper limit on production of soft tissue. I say 'upper limit' because we know that the PO_4 reaching the surface ocean is not fully utilized. This is especially true for the Southern Ocean where today only about one third of the PO_4 upwelled to the surface is removed bound in organic matter. The remainder is carried back to the interior with newly formed deep water.

The Benthic Foram Proxy for Deep Ocean O_2

The observation that benthic foraminifera are present in all open ocean sediments formed during the last 90 or so million years sets a limit on the ratio of the concentration of utilized PO_4 in the deep sea to that of dissolved oxygen in the water descending into the deep sea. The reason is that benthic foraminifera cannot survive in anoxic water. As about 175 moles of O_2 are utilized for every mole of PO_4 released in the deep sea, if the ratio of 175 times the concentration of utilized PO_4 to the concentration of preformed O_2 were greater than unity, parts of the deep ocean would go anoxic and benthic forams would not be present.

The amount of oxygen gas contained in newly formed deep water depends not only on temperature but also on the atmosphere's O_2 content. The waters entering today's very cold deep ocean are charged with about 350 μmol/liter of O_2. Fifty million years ago, the water in the deep ocean was about 10°C warmer than today's. Hence, if the atmosphere's O_2 content were the same as today's, the waters descending into the deep sea would have carried only 275 μmol per liter. In today's ocean, the ratio of saturation O_2 to 175 times total PO_4 is about two. Hence, were all the PO_4 utilized, large portions of the sea floor would be bathed in anoxic water. But, as only a fraction of the upwelling PO_4 is utilized, this does not happen. However, deep water in the northern Pacific dips very close to anoxia. Only about 5 percent of its initial O_2 remains.

The Strontium Isotope Record

As shown in Fig. 3-19, the ratio of ^{87}Sr to ^{86}Sr changes with time as the result of the production of ^{87}Sr by the decay of the long-lived radioisotope ^{87}Rb (half-life 50 billion years). Although, for the Earth as a whole, the increase of the ^{87}Sr to ^{86}Sr ratio created in this way has been quite small, that for its continental cratons has been sizable. The reason is that as the element rubidium is highly incompatible, it is highly enriched in volcanic melts. By this I mean that it is too large to fit comfortably into the lattices of the minerals that make up the Earth's mantle. Hence, when melting commences, rubidium is pushed out into the liquid phase. Consequently it is highly enriched over strontium in igneous rocks formed by partial melting. So, the Rb to Sr ratio in the Earth's granitic crust is much higher than that in the Earth's interior and that in sea floor basalts. Further, as the granitic cratons found on every continent formed billions of years ago, their strontium is disproportionally enriched in ^{87}Sr. Hence the 87 to 86 ratio in its strontium is on the average higher in the continental crust than in the Earth's mantle.

Strontium is added to the ocean via two routes: rivers and ridge crests. As the hydrothermal waters emanating from spreading centers derive their strontium from the newly formed basalt, they have mantle-like strontium isotope ratios. By contrast, the river input reflects the strontium isotope composition of the rocks being weathered on continents. Of the latter, limestones are the most important. As they formed in the ocean, limestones contain strontium that has been recycled through the ocean many times. However, rivers also contain strontium derived from old igneous rocks. Consequently river water has a somewhat higher ^{87}Sr to ^{86}Sr than hydrothermal waters. The isotopic composition of strontium in today's ocean lies in between that for these two inputs but somewhat closer to that for rivers. This suggests that about two thirds of its strontium entering the ocean was derived from rivers and one third from ridge-crest hydrothermal waters (Fig. 3-20).

Going back 500 million years, the strontium isotope record kept in limestone is surprisingly flat. It has ups and downs but no discernable long-term increase. One prominent

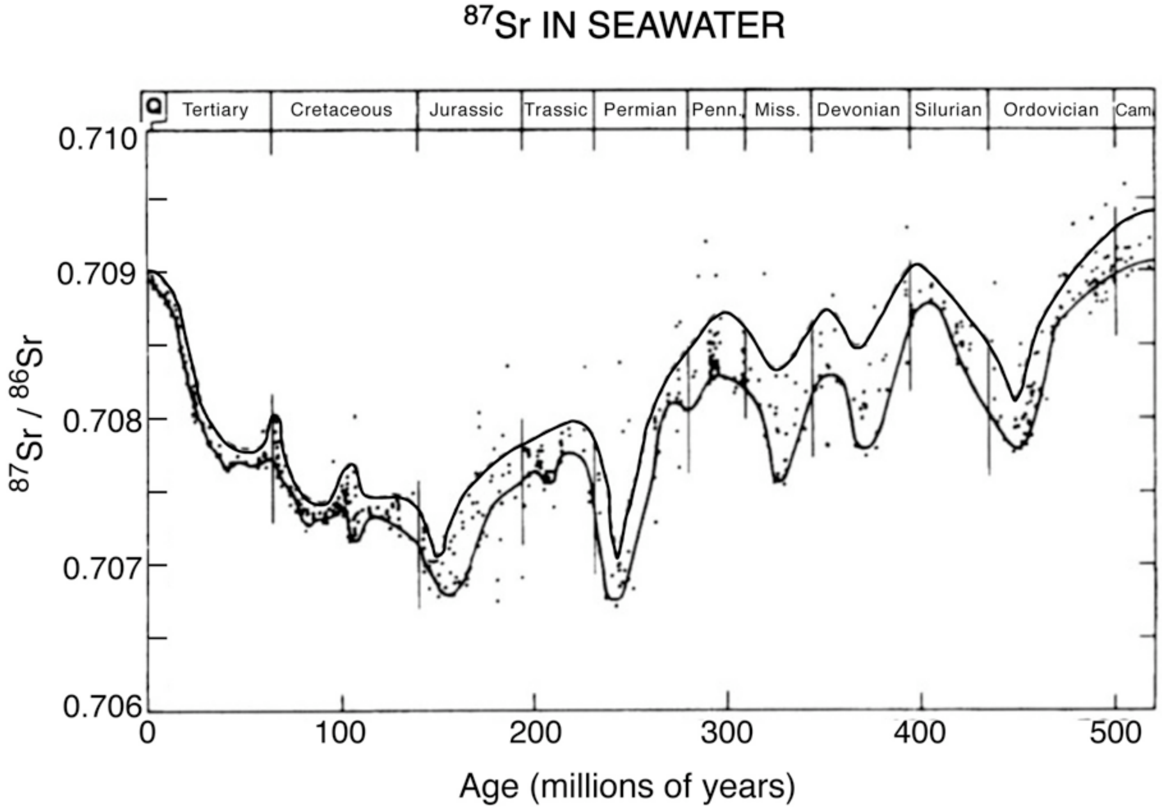


Figure 3-19. The record of the ^{87}Sr to ^{86}Sr in seawater as recorded in limestone. The dots represent the individual measurements. The solid lines outline the envelope of these results. Note that the range is much narrower for the last 100 million years than for earlier times. This likely reflects an increase in the extent of diagenesis with age.

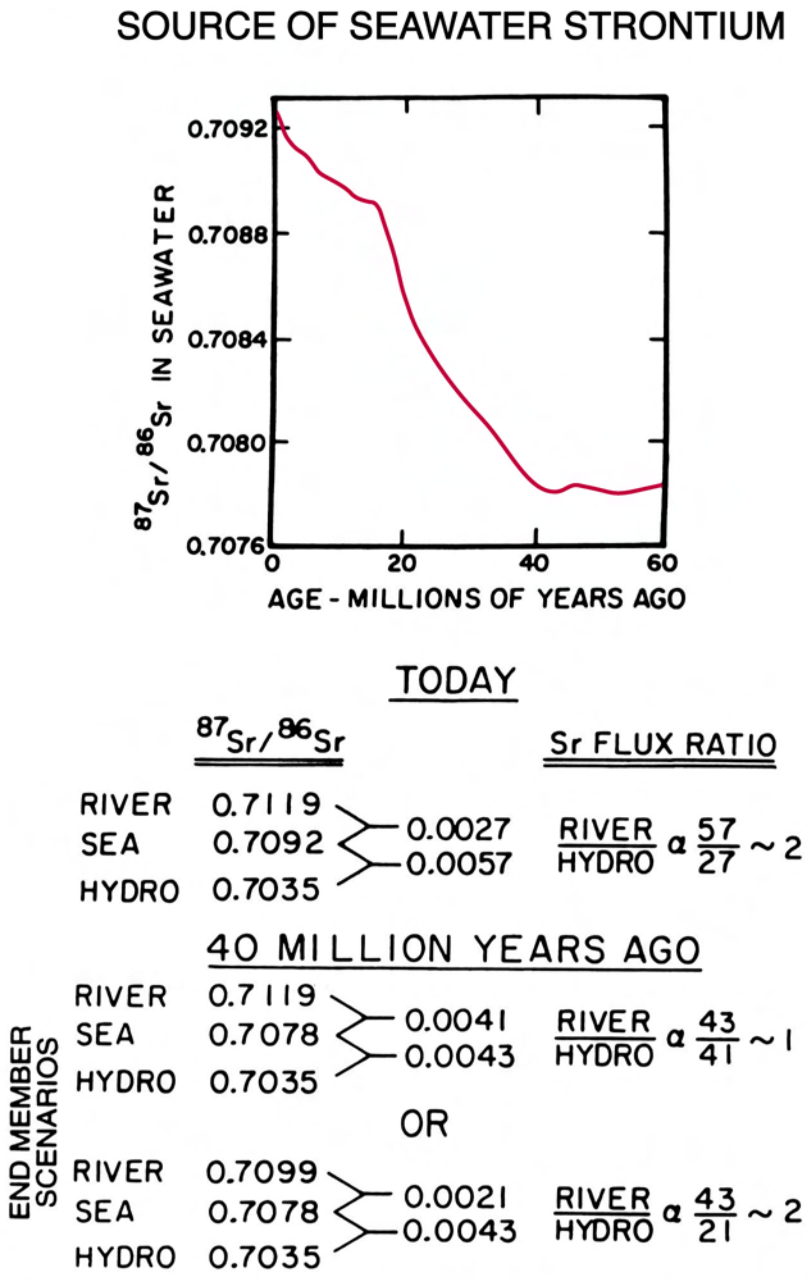


Figure 3-20. Forty million years ago, the ^{87}Sr to ^{86}Sr ratio in seawater commenced its largest Phanerozoic increase. Two scenarios have been put forward to explain this climb. One invokes an increase in the supply of strontium by rivers relative to that from ridge crests. The other invokes a large increase in the ^{87}Sr to ^{86}Sr ratio for the strontium carried by rivers draining the Himalayas. Both scenarios involve the collision between the Indian and Asian land masses as the initiator. To me only the isotopic scenario makes sense.

feature is the steep rise which commences about 40 million years ago. This was 10 or so million years after the time of the collision between the northward-drifting Indian continent and the Eurasia continent. Two quite different explanations for this rise have been given. Both involve the creation of the Himalayan mountain chain. One holds that its appearance increased the rate of continent weathering. If so, the isotope record tells us that before the collision, the strontium input from the continents must have been about the same as that from hydrothermal vents. Since 40 million years ago, it steadily increased until today it is now twice that from hydrothermal vents. The other explanation is that weathering of the Himalayas releases strontium with an unusually high component of ^{87}Sr. Indeed, the ^{87}Sr content of the strontium carried by Himalayan rivers is abnormally high. I favor the latter of these scenarios. As the rivers draining the Himalayas currently supply only 15 percent of the river supply, it is a large stretch to say that the creation of the Himalayas doubled the continental weathering rate.

One might ask why the ^{87}Sr to ^{86}Sr ratio in Himalayan rivers is unusually large. As pointed out by the late John Edmond, a geochemist who spent his career at MIT, the answer has to do with the metamorphism of granitic rocks resulting from their deep burial in association with the India-Asia collision. In the absence of such a metamorphism, the strontium released during the weathering of granites comes largely from plagioclase (Ca feldspar). As this mineral contains much strontium and little rubidium, it has little extra ^{87}Sr. By contrast, the micas and hornblendes rich in rubidium and poor in strontium are less easily weathered. During metamorphism, the high ^{87}Sr to ^{86}Sr strontium in micas and hornblendes is homogenized with the low ^{87}Sr to ^{86}Sr strontium in feldspars. Then when these granites are exhumed by uplift and exposed to weathering, this radiogenic strontium is released to the soil water rather than trapped in detritus. If this is the correct explanation, then the 10-million-year delay between the collision and the onset of the ^{87}Sr increase could be explained. It is the time required to exhume granites buried by the continental collision.

Looked at another way, as the rate of release of Ca from silicate rocks must match the rate of CO_2 release from the planet's interior, no increase in global weathering would be expected unless the input of CO_2 increased. If the weathering rate of silicate-bound Ca from the Himalayan region increased (and there was no increase in CO_2 delivery), then the rate of calcium delivery from the rest of the world must have correspondingly decreased.

Lithium Isotope Record

A surprise came when Florida State's Flip Froelich published a record of marine lithium isotope ratios covering the last 70 million years. He measured the ^{7}Li to ^{6}Li ratio in lithium contained in foraminifer shells (Fig. 3-21). It revealed a near linear 10 per mil increase in $\delta\ ^7$Li during the last 50 million years. The enrichment of ^{7}Li takes place during the formation of clay minerals. The light isotope (^{6}Li) is taken up with slight preference, leaving the unused lithium enriched in the heavy isotope (^{7}Li) clay when minerals are formed both in soils and in low temperature alteration of sea floor basalts. We know that this separation occurs on the continents because the lithium in river water is enriched in ^{7}Li. This being the case, one might postulate that the extent of fractionation has increased as the Earth has cooled. However, the change is likely too large to be explained in this way. As the δ^7Li for igneous rocks averages +5 per mil, the extent of fractionation would have to have increased from 17 per mil 50 million years ago to 27 per mil today.

Froelich's tentative explanation for this surprisingly large rise was that the intensity of chemical weathering steadily decreased over this period of time. By intensity of weathering, he meant the split between the fraction of a rock carried away in solution and that carried away as detritus. Today, the highest intensity of chemical weathering occurs in tropical areas such as South America's Guianas. There the soils consist mainly of the highly insoluble oxides iron and aluminum. The soluble cations Ca, Mg, K, and Na have been entirely leached out. In this situation all the lithium contained in the original rock is released. Hence it had an isotopic composition close to that in the parent material. At the

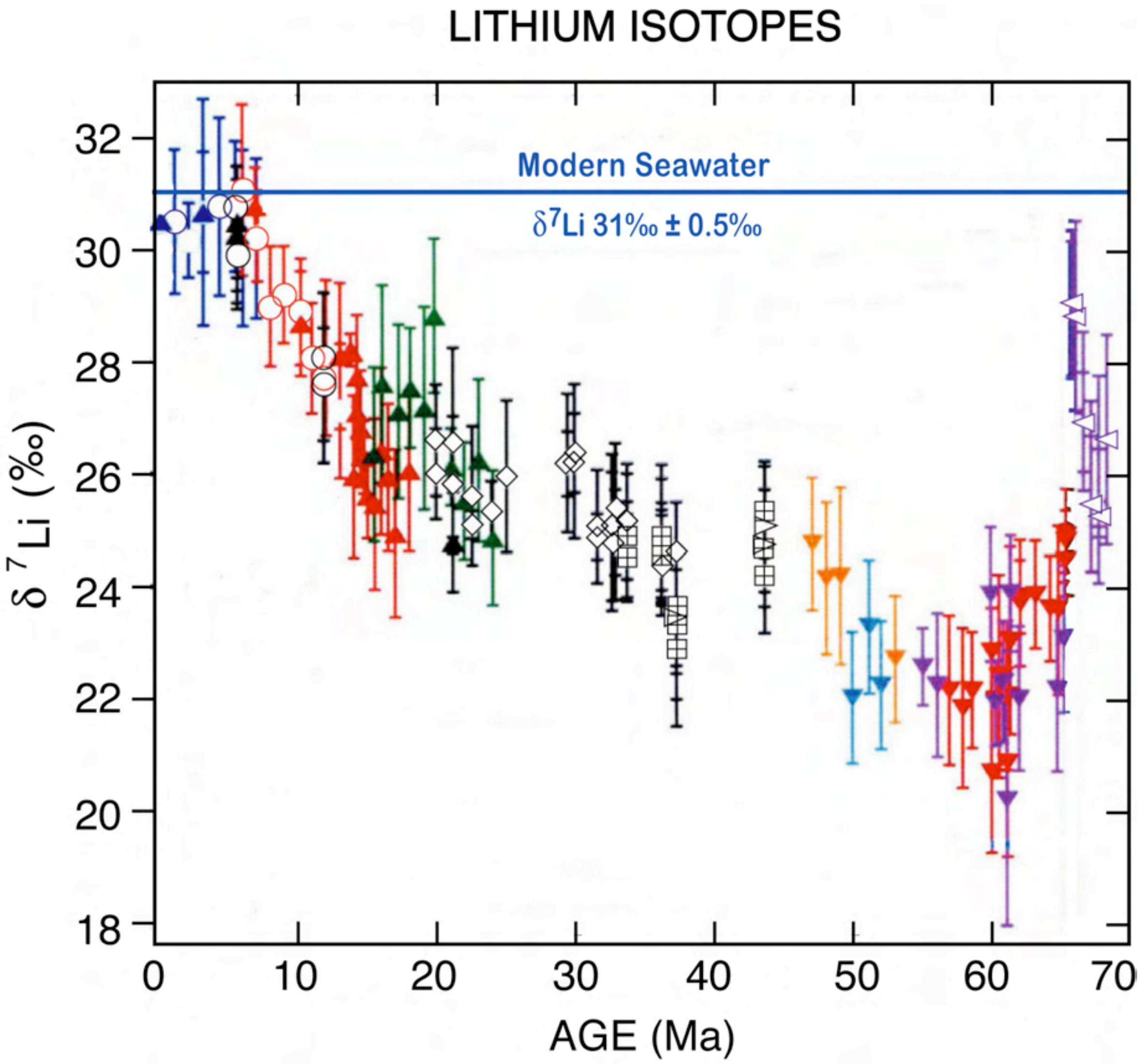


Figure 3-21. The Cenozoic evolution of the ratio of ^{7}Li to ^{6}Li in seawater as recorded in planktic foraminifer shells. The initial explanation for the increase in δ^7Li over the last 50 million years is that a decrease in the intensity of chemical weathering occurred. Partial weathering leads to the formation of clay minerals which preferentially take up ^{6}Li. Hence, the lithium released to river water is enriched in ^{7}Li (Froelich and Misra, 2014). However, far more research will be required before this rise can be fully understood. For example, how much of the change can be attributed to cooling (see similarity between the shape of the ^{7}Li and benthic ^{18}O trends, Figure 3-22).

other extreme is the largely mechanical weathering that occurs in frigid regions like Siberia. Under such conditions, clay minerals are formed. They take up the light lithium isotope relative to the heavy isotope. Hence the lithium which escapes is enriched in δ^7Li. So, one way to explain the rise was that 50 million years ago a much higher percentage of the lithium reaching the ocean came from lateritic soils.

To the extent reactions occurring in the ocean are important, the ratio of removal by low temperature to removal by high temperature, alteration of sea floor basalts and sediments is important. Only during low temperature, uptake would leave behind lithium enriched in its heavy isotope. Clearly, much more will have to be learned before we will be able to say why ocean lithium became 10 per mil heavier over the last 50 million years. Field studies akin to those out in Iceland (Pogge von Strandmann et al., 2006) and in New Zealand (Pogge von Strandmann and Henderson, in press) are essential to this quest.

The Oxygen Isotope Record

Our most valuable paleo temperature records come from oxygen isotope measurements on benthic foraminifera shells (Fig. 3-22). One might ask, isn't the same true for planktic foraminifera? The answer is no. One reason is that on multimillion–year timescales, their ^{18}O to ^{16}O ratio shifts toward equilibrium with the cold water in the pores of deep sea sediments. Also, although the oxygen isotope composition of deep ocean water is quite uniform, geographically that of surface water varies from place to place.

As marine limestones of all ages are available, it is conceivable that the ^{18}O to ^{16}O ratios they archive would provide a complete temperature record. But, unlike the benthic foraminifera shells in deep sea cores, limestones 'baked' during deep burial or recrystallized by exposure to meteoric water. As a result, they have become solid rock, i.e., limestones. Some of this limestone has been converted to dolomite. So much has happened to them that one might wonder if any of them have preserved their original oxygen isotope composition. In their attempt to find some that do, carbonate petrologists have focused in on the calcitic shells formed by brachiopods as the most promising candidates.

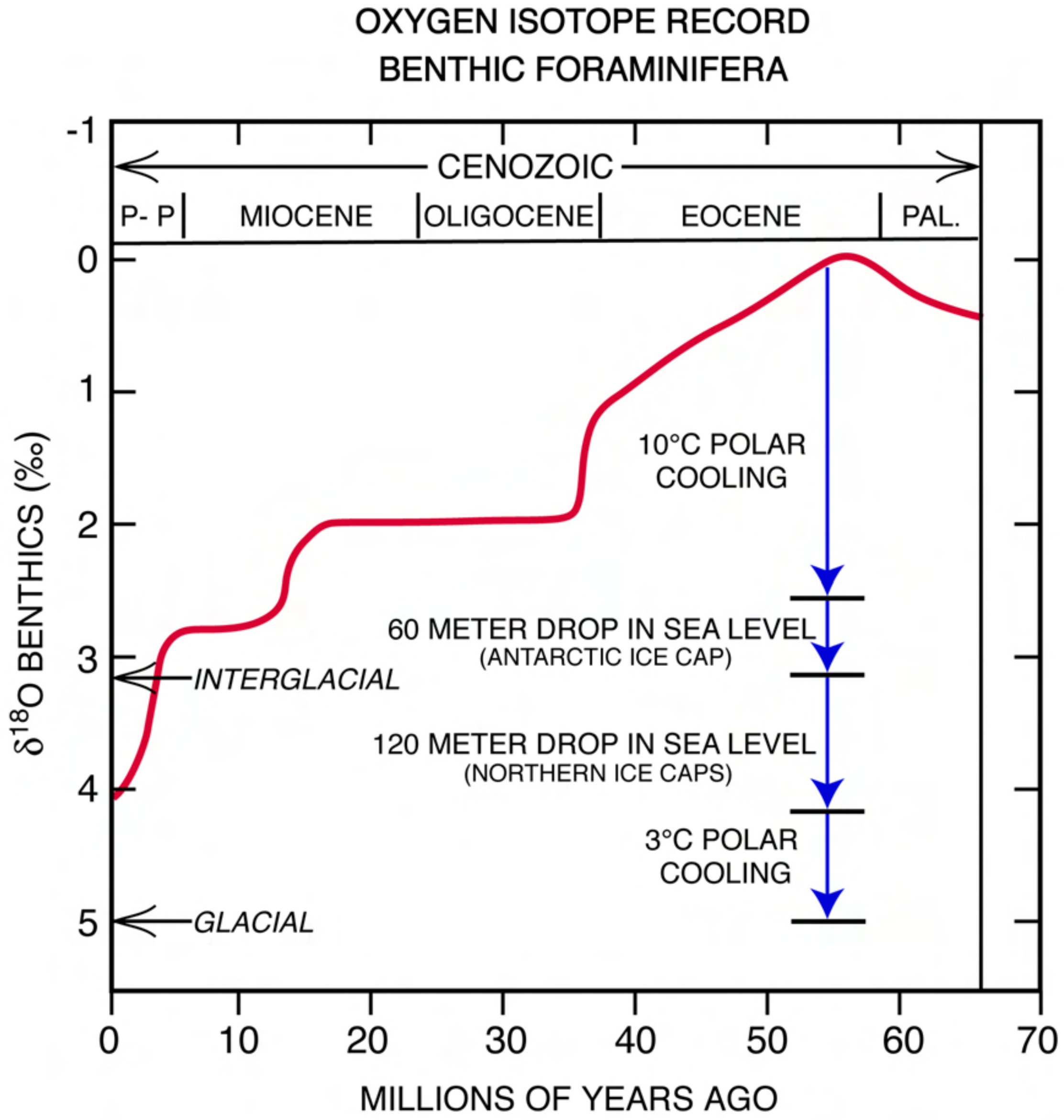


Figure 3-22. Record of ^{18}O to ^{16}O ratio for benthic foraminifera covering the entire Cenozoic. Although the variations resulting from glacial cycles have been smoothed, the peak glacial to peak interglacial range for the cycles of last half million years is indicated. The increase in $\delta^{18}O$ from the Cenozoic minimum (0‰) to that for the interglacials (3.2‰) is the result of the combination of a 10°C deep ocean cooling and the growth of the Antarctic ice cap. The 1.8‰ drop from peak interglacial to peak glacial is the result of a combination of the growth of the Canadian and Scandinavian ice sheets (1.0‰) and a cooling of the deep sea (0.8‰).

Even if perfectly preserved calcites could be found, a second problem remains. The isotopic composition of seawater may have changed. Further, it is not only the growth of ice sheets which causes these changes. On the time scale of 100 million years, the oxygen atoms in ocean water trade places with those in sea floor basalts. So, the question arises as to whether on these long time scales, the ocean's oxygen isotope composition has changed.

To date, thousands of oxygen isotope measurements have been made on Mesozoic and Paleozoic limestones and dolomites (Fig. 3-23). The great majority of them have lower ^{18}O to ^{16}O ratios than modern calcites. Three things could have contributed. First, the ocean may have been warmer. Second, the ^{18}O to ^{16}O ratio in seawater may have been lower. Third, recrystallization in the presence of ^{18}O-depleted meteoric water may have taken place. The debate about this has been hot and heavy for there has been no way to distinguish between the influence of ocean temperature and that of ocean isotope composition. Nor has there been any foolproof means of demonstrating that no diagenetic change occurred. Fortunately, clumped isotopes have come to the rescue. The abundance of mass 47 CO_2 (i.e., $^{12}C^{17}O^{18}O$) in calcite depends on growth temperature but is independent of the isotopic composition of the water in which the calcite formed. Hence, 'clumping' measurements on fossil brachiopods offer a means to separate the influences the temperature and the isotopic composition of seawater.

Many such measurements have been made by scientists working with John Eiler at Caltech. What they found is that, while some of the brachiopods yield environmentally reasonable clumping temperatures, others yield temperatures of several hundred degrees. The explanation appears to be that those recording unreasonably high temperatures had once been buried deep enough to have their clumping signature thermally reset.

In order to explore this possibility, laboratory heating experiments were conducted in order to determine the temperature dependence of the rate at which clumping is reset. The result was burial to temperatures above 200°C would lead to resetting. Further, this reordering would not be reversed when the limestone reappeared at the surface. Rather,

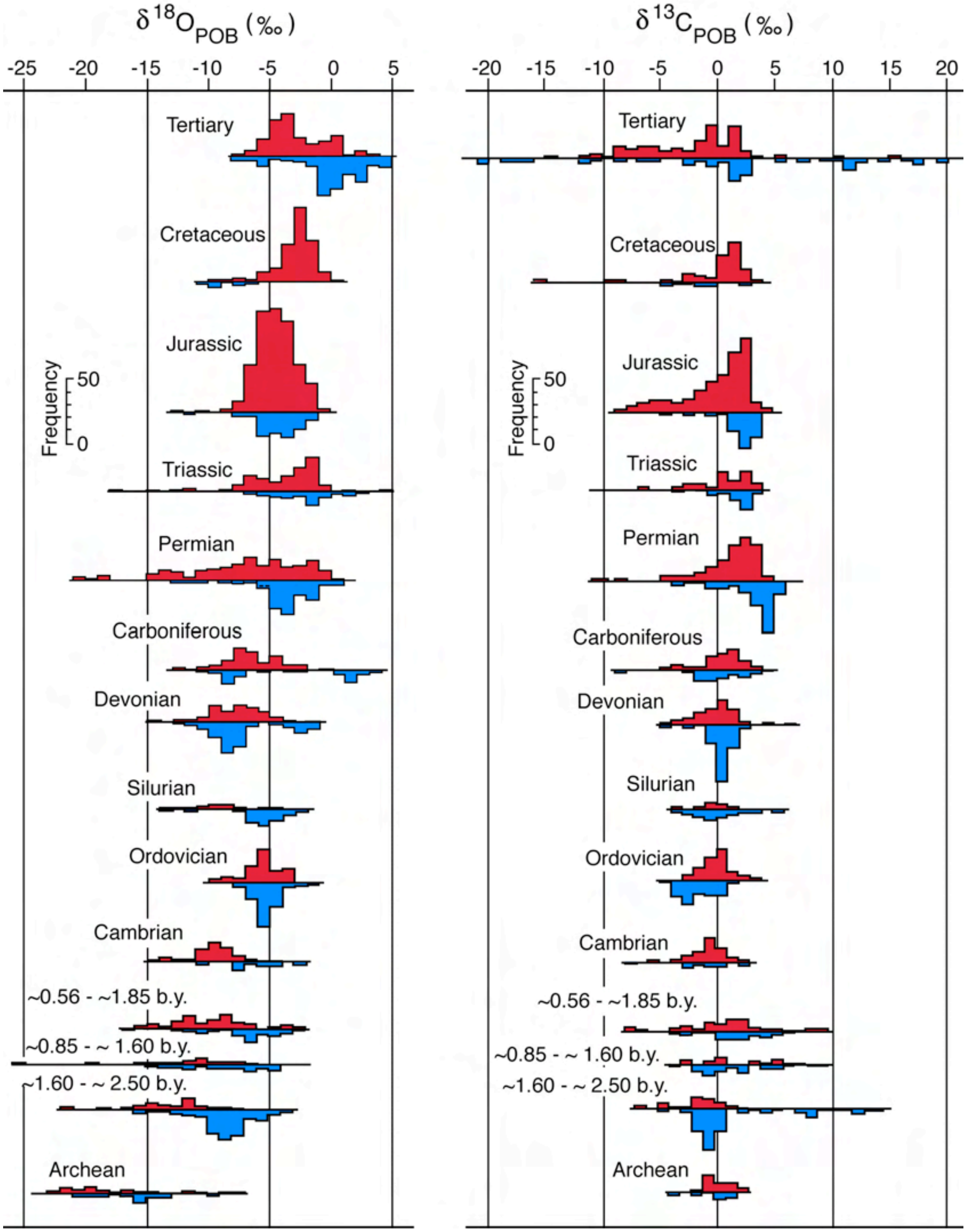


Figure 3-23. Compilation by Veizer and Hoefs (1976) of δ^{18}O and δ^{13}C on limestones (red histograms) and dolomites (blue histograms) extending back into the Archean. Note that while the results for carbon show no pronounced trend with age, those for oxygen show ever larger shifts to more negative values going back in time.

the high temperature imprint would be locked in.

With this in mind, Eiler's team concentrated on brachiopods from sediments that had not been deeply buried. Based on their clumping temperatures, they were able to calculate the oxygen isotope composition of the seawater in which brachiopods grew. They were pleased to find all these samples yielded seawater oxygen isotope compositions within the measurement error of todays. Hence they appear to have eliminated one of the three possible explanations for the low ^{18}O values in ancient brachiopods.

Assuming that their samples had not been isotopically altered by exposure to fresh water, they were then able to calculate paleo ocean water temperatures. They found values as high as 35°C. If correct, then the temperature was close to the upper limit for the survival of multicellular organisms. Above 38°C, the photosynthetic enzyme rubisco becomes inoperative. Without plant food, the entire web of living organisms would collapse. It has not.

The Salinity Record

Currently, more chloride is present in halite deposits and in sedimentary brines than in the ocean. As salt is being shuttled back and forth among these reservoirs, it would be surprising if the oceans salinity has not changed. Of interest is that if it were too high, it would have led to the extinction of salt-intolerant organisms or in the extreme, of all marine organisms.

Fortunately, there is a salinity proxy. Just as the air trapped in Antarctic ice allows the reconstruction of the atmosphere's CO_2 content, seawater trapped in bubbles in marine calcite offers a way to reconstruct the ocean's salt content. The reason is that there is a way to measure the salt content of these inclusions. It involves their freezing points. The saltier the water, the lower its freezing point. For today's seawater it is -1.8°C. Paleo-salinity measurements are made by observing frozen seawater inclusions under a microscope as they slowly warm. The temperature at which they melt yields the salinity. However, as the inclusions of calcite are tiny, it's not so easy to do. Tim Lowenstein, of SUNY Binghamton, has recently taken up this challenge. He has preliminary results which suggest that Devonian and Cambrian seawater had salinities similar to todays. Clearly, much more will be done to extend and to validate this approach.

Additional Proxies

Coming on line during the last decade or so are a whole set of new proxies. Advances in mass spectrometry make it possible to measure isotope ratio changes at the 0.1 per mil level. As is the case for lithium, during chemical reaction involving mineral formation at earth surface temperatures, the light isotope of higher mass elements such as Sr, Ca and Mg are preferentially incorporated. Even larger fractionations take place when elements such as Fe and Cr undergo oxidation state changes.

References for Chapter 3

Berner, R. A., S. T. Petsch, J. A. Lake, D. J. Beerling, B. N. Popp, R. S. Lane, E. A. Laws, M. B. Westley, N. Cassar, F. I. Woodward, and W. P. Quick (2000), Isotope fractionation and atmospheric oxygen: Implications for Phanerozoic O_2 evolution, *Science*, *287*, 1630-1633, doi: 10.1126/scinece287.5458.1630.

Berry, J., J. H. Troughton, O. Bjőrkman (1972), Effect of oxygen concentration during growth on carbon isotope discrimination in C_3 and C_4 species of Atriplex, *Carnegie Institution Yearbook*, *71*, 158-161.

Brennan, S.T., T. K. Lowenstein, and D. I. Cendón (2013), The major-ion composition of Cenozoic seawater: The past 36 million years from fluid inclusions in marine halite, *Am. J. Sci.*, *313*, 713-775, doi: 10.2475/082013.01.

Broecker, W., and J. Yu (2011), What do we know about the evolution of Mg to Ca ratios in seawater? *Paleoceanography*, *26*, PA3203, doi: 10.1029/2011PA002120.

Coggon, R. M., D. A. H. Teagle, C. E. Smith-Duque, J. C. Alt, M. J. Cooper (2010), Reconstructing past seawater Mg/Ca and Sr/Ca from mid-ocean ridge flank calcium carbonate veins, *Science*, *327*, 1114-1117.

Coggon, R. M., D. A. H. Teagle, and T. D. Jones (2011), Comment on "What do we know about the evolution of Mg to Ca ratios in seawater?" by Wally Broecker and Jimin Yu, *Paleoceanography*, *26,* PA3224, doi: 10.1029/2011PA002186.

Franks, P. J., D. L. Royer, D. J. Beerling, P. K. Van de Water, D. J. Cantrill, M. M. Barbour, and J. A. Berry (2014), New constraints on atmospheric CO_2 concentration for the Phanerozoic, *Geophys. Res. Lett.*, *41,* doi: 10.1002/2014GL060457.

Froelich, F., and S. Misra (2014), Was the Late Paleocene-Early Eocene hot because Earth was flat? *Oceanography, 27*, 37-49.

Hayes, J. M., H. Strauss, A. J. Kaufman (1999), The abundance of ^{13}C in marine organic matter and isotopic fractionation in the global biogeochemical cycle of carbon during the past 800 Ma, *Chemical Geology*, *161*, 103-125.

Holser, W. T., and I. R. Kaplan (1966), Isotope geochemistry of sedimentary sulfates, *Chemical Geology*, *1*, 93-135.

Hönisch, B, and N. G. Hemming (2005), Surface ocean pH response to variations in pCO2 through two full glacial cycles, *Earth Planet. Sci. Lett., 236,* 305-314.

Kent, D. V., and G. Muttoni (2013), Modulation of late Cretaceous and Cenozoic climate by variable drawdown of atmospheric pCO_2 from weathering of basaltic provinces on continents drifting through the equatorial humid belt, *Clim. Past*, *9*, 525-546, doi: 10.5194/cp-9-525-2013.

Misra, S., and P. N. Froelich (2012), Lithium isotope history of Cenozoic seawater: Changes in silicate weathering and reverse weathering, *Science*, *335*, 818-822.

Linhoff, B. S., P. C. Bennett, T. Puntsag, and O. Gerel, (2011), Geochemical evolution of uraniferous soda lakes in Eastern Mongolia, *Eviron. Earth Sci.*, *62*, 171-183, doi: 10.1007/s12665-010-0512-8.

Pälike, H. *et al.* (2012), A Cenozoic record of the equatorial Pacific carbonate compensation depth, *Nature*, *448*, 609-614, doi: 10.1038/nature11360.

Paris, G., J. Gaillardet, and P. Louvat (2010), Geological evolution of seawater boron isotopic composition recorded in evaporites, *Geology*, *38*(11), 1035-1038, doi: 10.1130/G31321.1.

Paytan, A., M. Kastner, D. Campbell, and M. H. Thiemens (2004), Seawater sulfur isotope fluctuations in the Cretaceous, *Science*, *304*, 1663-1665, doi: 10.1126/science.1095258.

Pogge von Strandmann, P. A. E., K.W. Burton, R. H. James, P. van Calsteren, S. R. Gislason, and F. Mokadem, (2006), Rivering behavior of uranium and lithium isotopes in an actively glaciated basaltic terrain, *Earth Planet. Sci. Lett.*, *251*, 134-147.

Pogge von Strandmann, P. A. E., and G. Henderson (2015, in press), The Li isotope response to mountain uplift, *Geology*, doi: 10.1130/G36162.1.

Raitzsch, M., and B. Hönisch (2013), Cenozoic boron isotope variations in benthic foraminifers, *Geology, 41*(5), 591-594, doi: 10.1130/G34031.1.

Strauss, H. (1997), The isotopic composition of sedimentary sulfur through time, *Palaeogeo. Palaeoclim., Palaeoecol.*, *132*, 97-118.

Tappert, R., R. C. McKellar, A. P. Wolfe, M. C. Tappert, J. Ortega-Blanco, and K. Muehlenbachs (2013), Stable carbon isotopes of C3 plant resins and ambers record changes in atmospheric oxygen since the Triassic, *Geochim. Cosmochim. Acta*, *121*, 240- 262.

Veizer, J., and J. Hoefs (1976), the nature of O^{18}/O^{16} and C^{13}/C^{12} secular trends in sedimentary carbonate rocks, *Geochim., Cosmochim. Acta*, *40*, 1387-1395.

Wortmann, U. G., and A. Paytan, (2012), Rapid variability of seawater chemistry over the past 130 million years, *Science*, *337*, 334-336.

Chapter 4
Oxygen Appears

Only for the last 10 percent of Earth history do we have a detailed stratigraphic record which allows the precise correlation of events across the planet. This record is based on the superposition of sediment with much help from the appearances and disappearances of marine species as recorded in the fossil record. This ordering of Earth events was established long before it was possible to determine absolute ages. Now thanks to highly accurate geochronometers based on the decay of the long-lived isotopes ^{40}K, ^{87}Rb, ^{235}U, and ^{238}U and of the cosmogenic isotopes ^{10}Be and ^{14}C, we have not only the sequence of events but also accurately dated tie points extending all the way back in time.

During the first 85 percent of Earth history, the life on Earth was single celled. As these micro-organisms made no hard parts, there is no fossil-based stratigraphy. Not only does the absence of fossils make it more difficult to sequence the rock record, but also makes it far more difficult to tease out information concerning the Earth's climate. Beyond the fact that sediments deposited from water are present throughout the record, by comparison with the last 700 million years, we know very little.

For the Earth's first two billion years (4.5 to 2.4 x 10^9 years) we have very little to go by. As photosynthetic algae had not yet evolved, there was no O_2 in the atmosphere. But, as volcanoes must have been belching forth CO_2 and rivers must have been delivering Ca to the ocean, there must have been deposition of $CaCO_3$ on the sea floor. However, in the absence of O_2, iron would have been quite soluble. So a portion of the CO_2 was deposited as iron carbonate. Presumably the throughput was governed by the atmosphere's CO_2 content. It kept the planet warm enough and wet enough to supply the calcium and iron needed to match the input of CO_2. As sediments deposited from water are present, it appears that at least low latitude temperatures were above the freezing point.

Starting about 3.5 billion years ago, evidence for primitive life in the form of cell walls is found in sediments. This suggests that the Earth as a whole was not too hot to allow life to exist. Put another way, we have no evidence that the temperature of our planet strayed outside the range it has occupied for the last half billion years. This makes sense because this is the range necessary to match the CO_2 emitted from volcanoes with cations weathered from continental silicate rock.

Two and one half billion years ago oxygen not only stepped onto the stage but began to impact the chemistry of both the atmosphere and ocean. Evidence for its appearance initially came from the element iron. When dissolved in water in the presence of oxygen, iron is in its oxidized form Fe_2O_3. In this form it is highly insoluble. However, in an oxygen-free environment, it is in its reduced form FeO. As such it is highly soluble. In accord with conditions throughout the solar system, early on conditions on Earth were highly reducing. Hence, at that time the ocean likely had concentrations of Fe^{++} comparable to those of Ca^{++} and Mg^{++}.

What is clear from the Precambrian record is that early on, sediments rich in iron were common (Fig. 4-1). Then midway through this era, they disappeared from the record. As the ability to obtain accurate radiometric ages improved, it became clear that the transition occurred close to 2.4 billion years ago.

As it takes very little O_2 to push the ocean from an iron-reducing to an iron-oxidizing state, one might ask why this transition didn't occur much earlier. Clearly, it had to await the evolution of organisms capable of photosynthesis. They appear in the fossil record at about this time. Of course, the buildup of O_2 could not occur until the reduced iron and sulfur present at the Earth's surface were oxidized.

It should be mentioned that not everyone is comfortable with this scenario. Iron formations have a complex stratigraphy and a complex mineralogy. Not all the iron is reduced. Further, after disappearing from the record two billion or so years ago, they made a brief reappearance during the late Precambrian.

Figure 4-1. Picture of a banded (i.e. layered) iron formation.

Fortunately a dramatic verification of this scenario has appeared. It had to do with a discovery made by UC San Diego scientist, Mark Thiemens. He surprised the world of isotope geochemistry by demonstrating that mass independent fractionation of isotopes occurs during chemical reactions among gases. Up until his discovery, it was thought that all such separations were mass dependent. For example, ^{18}O was separated from ^{16}O by twice as much as ^{17}O. But Thiemens showed that for some gaseous reactions symmetry trumped mass. The asymmetric $^{18}O^{16}O$ and $^{17}O^{16}O$ act differently than symmetric $^{16}O^{16}O$. Today, the O_2 in the atmosphere has a ^{17}O content which departs slightly from the mass dependent trend that characterizes Earth materials. Unlike the composition trend for water which is slavishly mass dependent, reactions in the atmosphere involving ozone and O_2 are dictated by molecular symmetry rather than mass.

Picking up on this, Farquhar and Thiemens used mass independent fractionation to demonstrate that the oxidation state of the atmosphere dramatically changed 2.5 billion years ago. In today's atmosphere, gases containing sulfur are rare. H_2S is rapidly oxidized to SO_2, and SO_2 is equally rapidly converted to H_2SO_4 aerosols. As these aerosols serve as nuclei for rain drops, they are rapidly removed from the atmosphere. Although mass independent fractionation likely occurs, this tiny side loop of the Earth's sulfur cycle does not leave any imprint in the isotopic composition of sulfide minerals. However, were O_2 absent, gases containing sulfur could have been present in appreciable amounts. So Farquhar and Thiemens went about looking for mass independent separation of isotopes ^{34}S and ^{36}S from the dominant isotope ^{32}S. They did so by analyzing the isotopic composition of sulfur-bearing minerals of sedimentary origin. They hit pay dirt (Fig. 4-2). For sulfur-bearing minerals older than 2.5 billion years, they found deviations from the mass-dependent fractionation trend. But in those younger than 2.5 billion years in age, these anomalies disappeared. So sulfur is telling us the same story as iron. Before 2.5 billion years ago, both elements were present in their reduced form. After 2.5 billion years ago, both were present in their oxidized form.

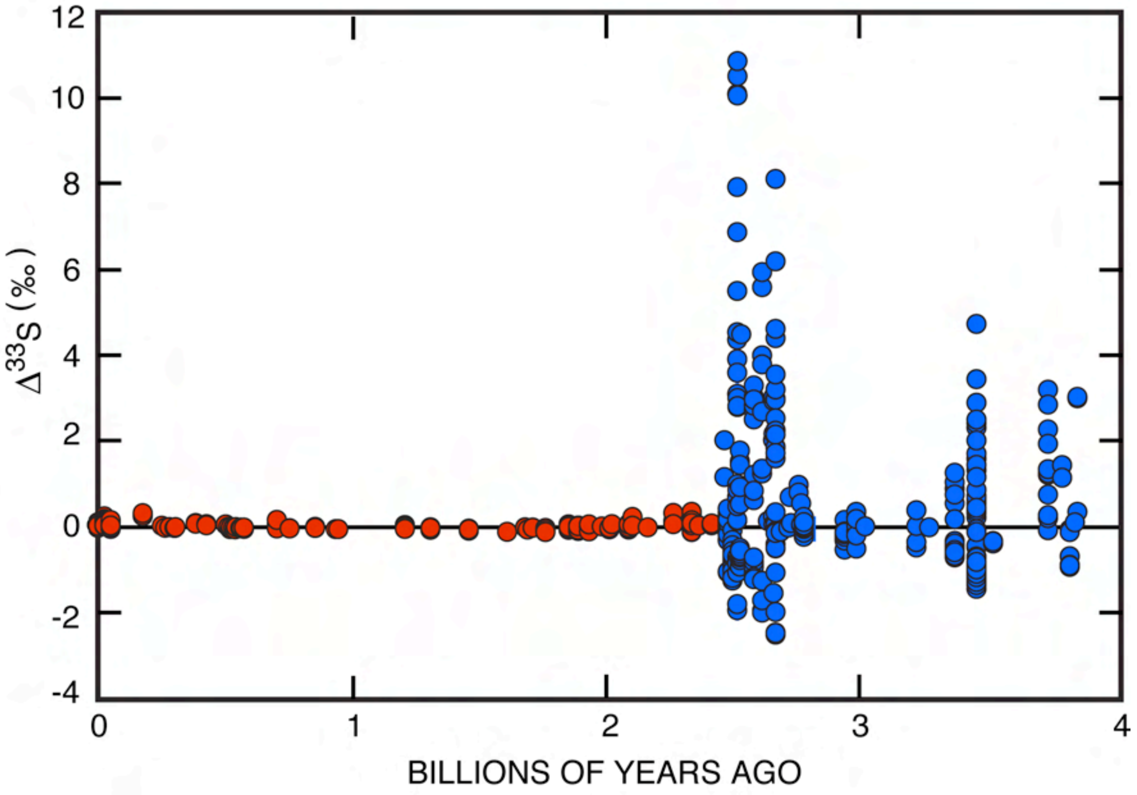


Figure 4-2. Sulfur isotope measurements on sedimentary sulfide and sulfate deposits reveal that an important change occurred 2.4 billion years ago. Before that time there were deviations resulting from mass independent fractionation (blue dots). Afterward they disappeared (red dots). The explanation is that O_2 gas made its first appearance in the atmosphere at that time. In the absence of O_2 the atmosphere contained sizable amounts of H_2S and SO_2. In its presence of O_2 these gases virtually disappeared from the atmosphere. It was the reactions among the gases that gave rise to mass independent separation of the sulfur isotopes (Farquhar et al., 2010). $\Delta^{33}S$ is the deviation of its ratio from that expected if only mass-dependent fractionation were operative (as expected if the ^{33}S offset were one quarter that between ^{32}S and ^{36}S or one half that between ^{32}S and ^{34}S).

Although it's difficult to say just how, the appearance of O_2 must have had an impact on the carbon cycle. The slack created when iron was no longer available to pair with CO_2 must have been taken up by calcium. Thus weathering rates may have been forced to increase. More CO_2 in the atmosphere?

One might suspect that once O_2 appeared its content would have undergone a continuous rise. However Planavsky et al. (2014) make a case that it remained very, very low until about 800 million years ago. They base their case on the isotopic composition of the element chromium in shales. In the absence of O_2, chromium is present only in its reduced form, Cr(III). But when O_2 is present, it can be converted to its oxidized form, CR(VI). Accompanying oxidation is a large (up to 10‰) enrichment of the heavy isotope ^{53}Cr. Further, in its oxidized form, chromium is more soluble than in its reduced form. This soluble chromium is released from soils and some is incorporated in shales. As shown in Fig. 4-3, shales older than 800 million years have δ^{53}Cr values identical to those for igneous rocks. Those younger than this have δ^{53}Cr values up to 2 per mil higher than those for igneous rocks. As the time of this switch corresponds to that of the first appearance of various eukaryotic organisms, the suggestion is that the appearance of these organisms awaited the rise of O_2 in our atmosphere.

Another indication that a substantial rise in O_2 occurred during the Proterozoic is the jump in a molybdenum content in black shales about 0.6 billion years ago (Fig. 4-4). In its reduced form, this element is highly insoluble. Hence, the increase in its abundance in black shales is thought to herald this increased availability of O_2**.**

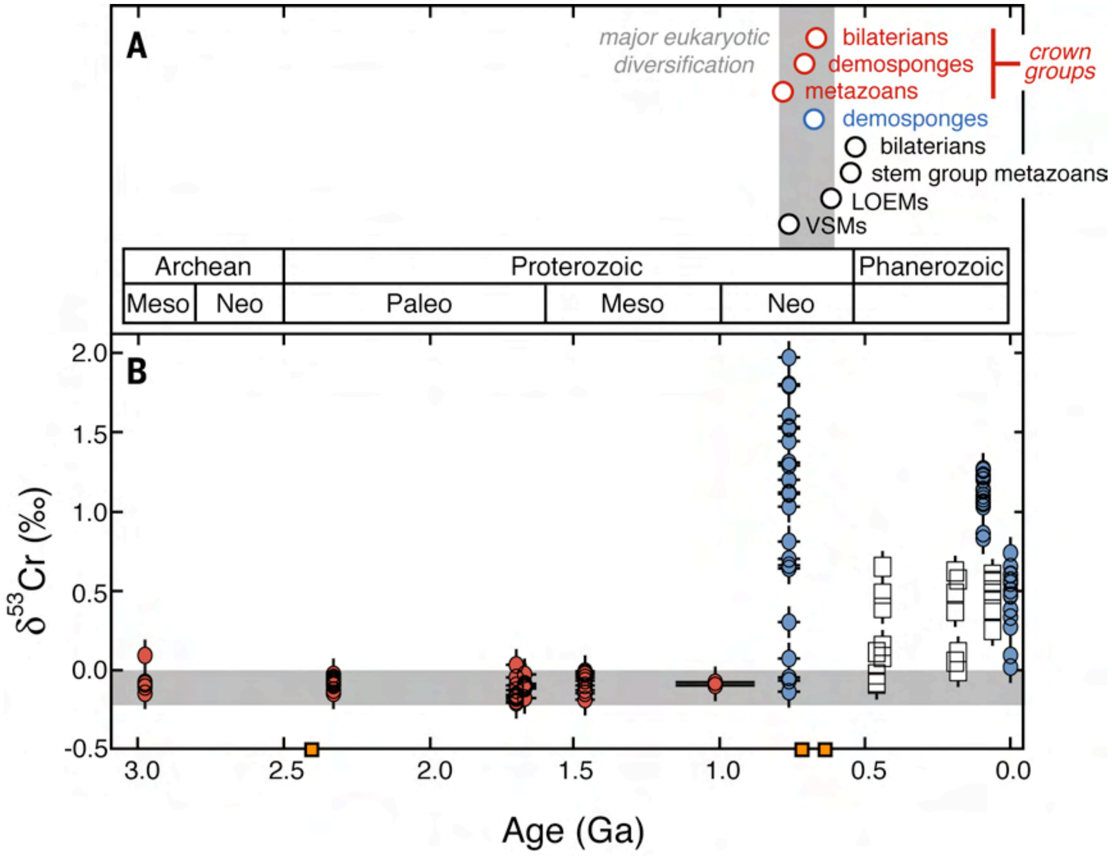


Figure. 4-3. Prior to 0.8 billion years ago, isotopic composition of the element chromium in shales was the same as that in igneous rocks. After that time higher increase in the ^{53}Cr to ^{52}Cr ratio are found (Planavsky et al., 2014). This increase is thought to mark the appearance of O_2 in the atmosphere. If so, then it makes sense that the evolution of multicellular organisms awaited this O_2 increase. As shown, 8 different groups of multicellular organisms made their appearance during the 0.3 Ga following the rise in O_2.

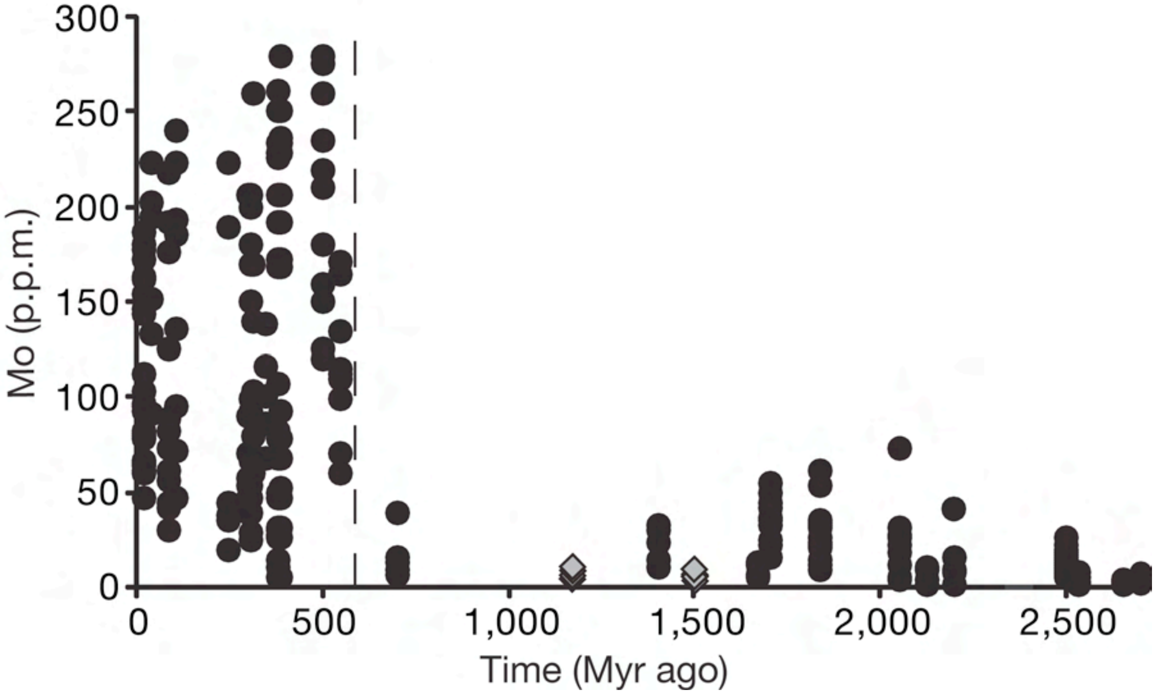


Figure 4-4. Molybdenum content of black shales formed during the last 2.7 billion years (Scott et al., 2008). In order for authigenic molybdenum to exist, small amounts of it must have been present in the atmosphere and ocean. The major increase after 0.6 billion years suggests a substantial jump in O_2 content.

References for Chapter 4

Anbar, A. D. *et al.* (2007), A whiff of oxygen before the Great Oxidation Event? *Science*, *317,* 1903-1906.

Bekker, A., H. D. Holland, P.-L Wang, D. Rumble III, H. J. Stein, J. L Hannah, L. L. Coetzee, and N. J. Beukes (2004), Dating the rise of atmospheric oxygen, *Nature*, *427*, 117-120.

Farquhar, J., H. Bao, and M. Thiemens (2000), Atmospheric influence of Earth's earliest sulfur cycle, *Science*, *289*, 756-758.

Farquhar, J., N. Wu, D. E. Canfield, and H. Oduro (2010), Connections between sulfur cycle evolution, sulfur isotopes, sediments, and base metal sulfide deposits, *Economic Geology, 105*, 509-533.

Holland, H. D. (2002), Volcanic gases, black smokers and the Great Oxidation Event, *Geochim, Cosmochim. Acta, 66*, 3811-3826.

Lyons, T. W., C. T. Reinhard, and N. J. Planavsky (2014), The rise of oxygen in Earth's early ocean and atmosphere, *Nature*, *506*, 307-315, doi: 10.1038/nature13068.

Planavsky, N. J., C. T. Reinhard, X. Wang, D. Thomson, P. McGoldrick, R. H. Rainbird, T. Johnson, W. W. Fischer, and T. W. Lyons (2014), Low Mid-Proterozoic atmospheric oxygen levels and the delayed rise of animals, *Science, 346*, 635-638.

Scott, C., T. W. Lyons, A. Bekker, Y. Shen, S. W. Poulton, X. Chu, and A. D. Anbar (2008), Tracing the stepwise oxygenation of the Proterozoic ocean, *Nature, 452*, 456-459, doi: 10.1038/nature06811.

Chapter 5

The Earth Freezes

The second Precambrian episode of note was a spectacular one involving huge swings in Earth temperature. It is recorded in the carbon isotope record kept in limestone and dolomite (Fig. 5-1). Between 800 million years ago and 540 million years ago, the ^{13}C to ^{12}C ratio underwent several large dips. Three of these dips culminated in snowball episodes during which the Earth's surface appears to have been frozen from pole to equator. The recovery from the last of these carbon isotope plunges marked the end of the Precambrian ushering in a world in which multi-celled plants and animals had primary roles (Fig. 5-1).

Until about 30 years ago, these deposits were poorly dated and controversial. Then Harvard's Paul Hoffman and Dan Schrag stepped in and pushed the idea that they did indeed record Earth freeze-ups. They coined the term Snowball Earth. This initiated rapid progress toward better documentation. Uranium-lead ages were obtained on zircons contained in volcanic ashes (Fig. 5- 2). Strontium isotope measurements allowed deposits from isolated locales to be placed in stratigraphic order (Fig. 5-3) and paleo-magnetic-based latitude reconstructions made clear that the tropics were glaciated (Fig. 5-4). Finally, the carbon isotope record screams out that the Earth's carbon cycle must have gone haywire.

To me the carbon isotope plunges speak loudly of catastrophic failures in the control system for carbon. To freeze the Earth requires that the atmosphere's CO_2 level dropped to an all-time low level. But, as we have so little to go on, any scenario put forward to explain why this happened remains speculative.

The interpretation of the $\delta^{13}C$ drops which occurred is, however, highly contested. One group claims that they are so highly impacted by secondary alteration that they have no story to tell. Another group, while admitting that the record is imperfect, claim that, as the carbon isotope ratios present a generally consistent picture, they must contain important clues as to what caused the freeze-ups. Recently, a group at Harvard have taken an important step toward determining

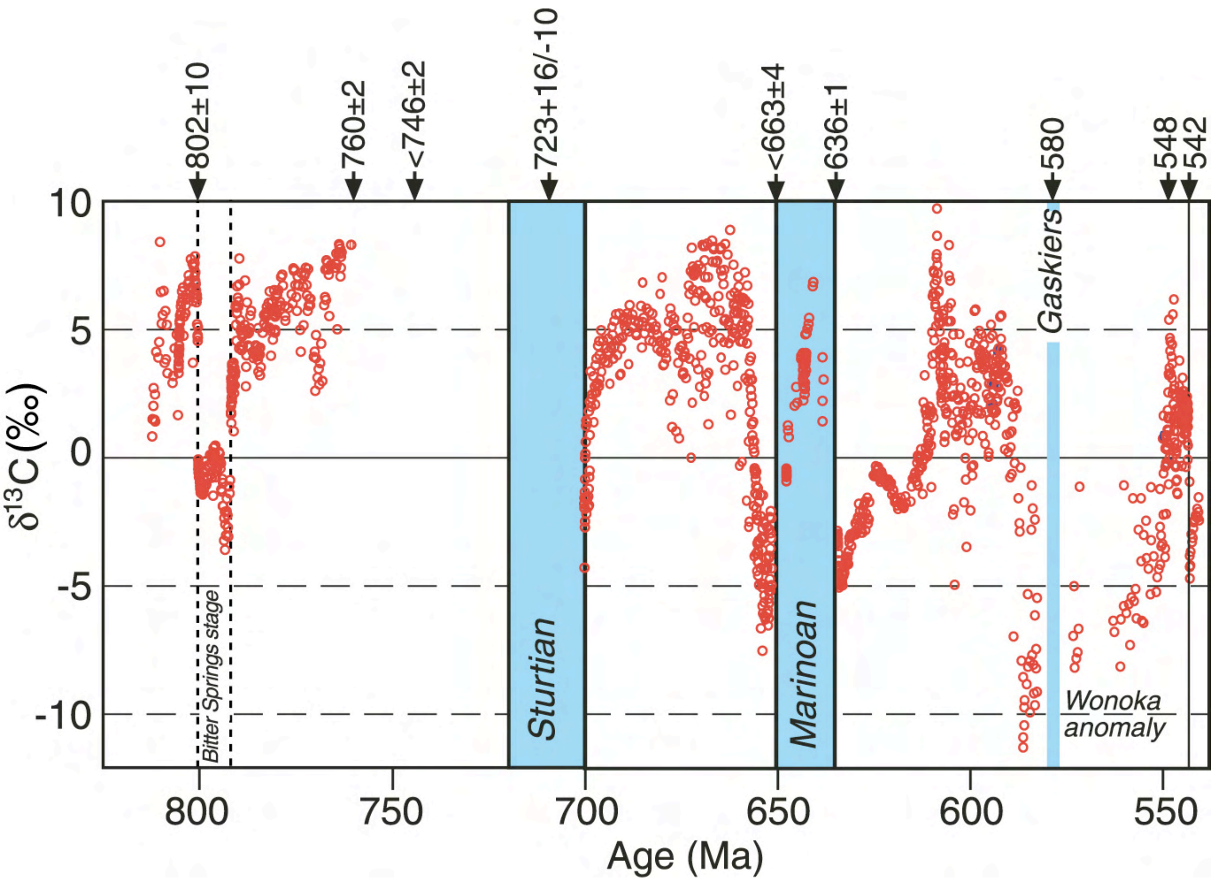


Figure 5-1. Summary of the carbon isotope record for limestone from four locales: Svalbard, Namibia (Halverson et al., 2005), Oman, and Australia. Uranium-lead ages obtained on zircons contained in volcanic ash layers provide an accurate chronology for these events. Two of the dips in $\delta^{13}C$ (the Sturtian and Marinoan) correspond to well-documented snowball earth events. Of particular interest, the first of the carbon isotope dips (the Bitter Springs) appears not to have culminated in a snowball event.

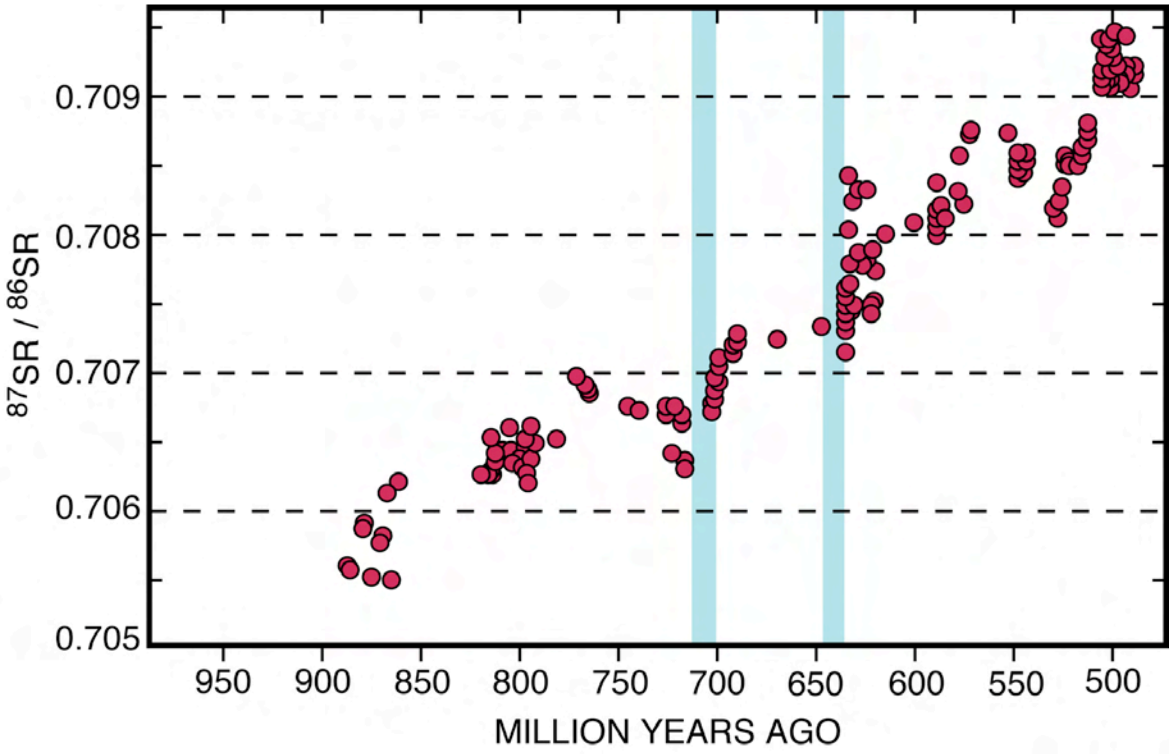


Figure 5-2. Strontium isotope record (Halverson et al., 2010) for the time interval in which the δ^{13}C dips occurred. The near steady 400 million-year-long climb of the ^{87}Sr to ^{86}Sr ratio allows the carbon isotope records from diverse locales to be correlated. Note that after both of the prominent snowball events (gray bars), there is a steep rise in the ratio. One explanation for this would be that the intense chemical erosion associated with the warm temperatures and acid rain changed the balance between the ridge crest hydrothermal component (low 87/86) relative to that from continental weathering (high 87/86) in favor of the latter.

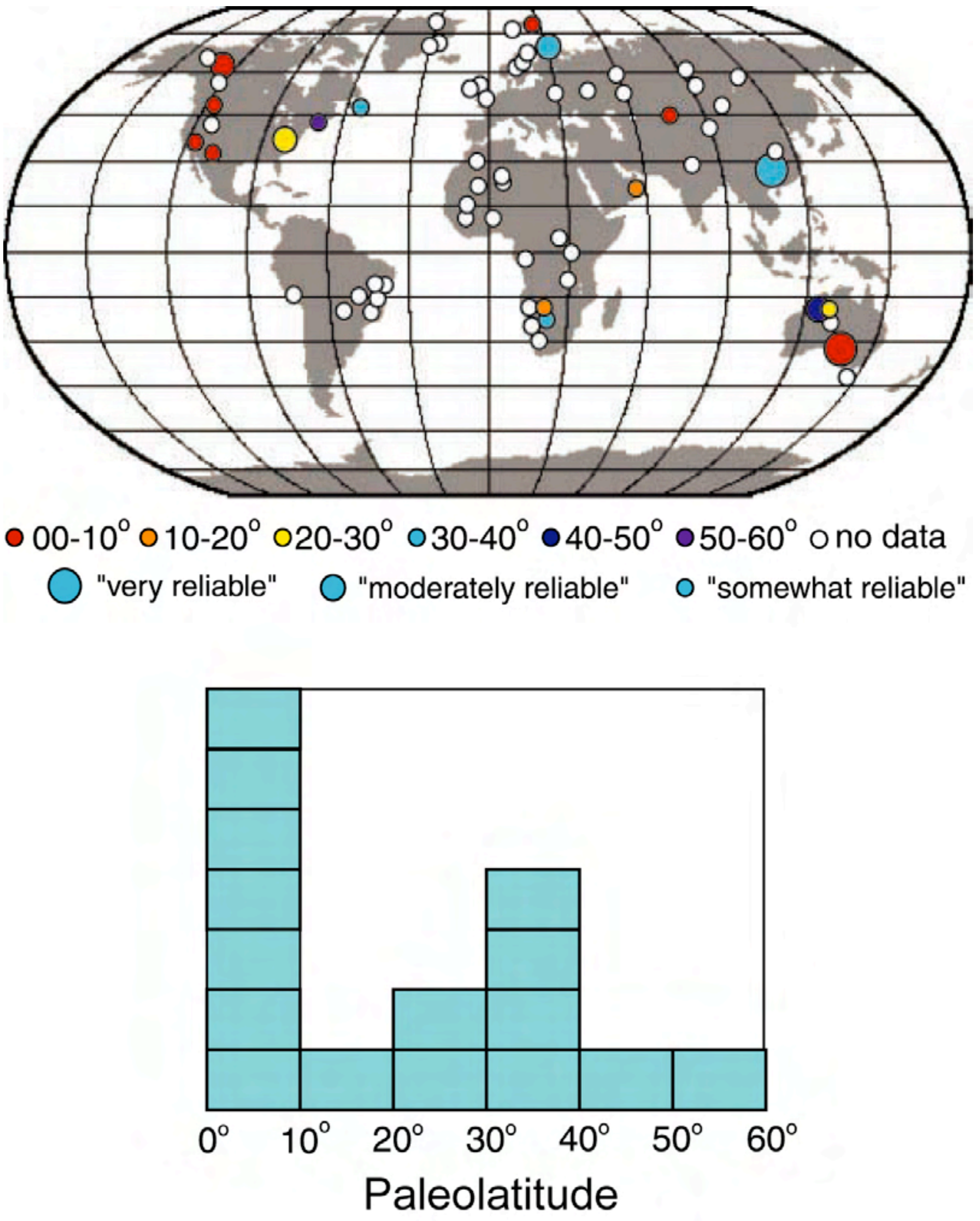


Figure 5-3. Global distribution of Neoproterozoic glacial deposits. Also shown is a histogram of the paleo-latitude distribution of the sixteen locales which yield useable magnetic vectors. Seven of these lie within 10 degrees of the equator (Schrag et al., 2002).

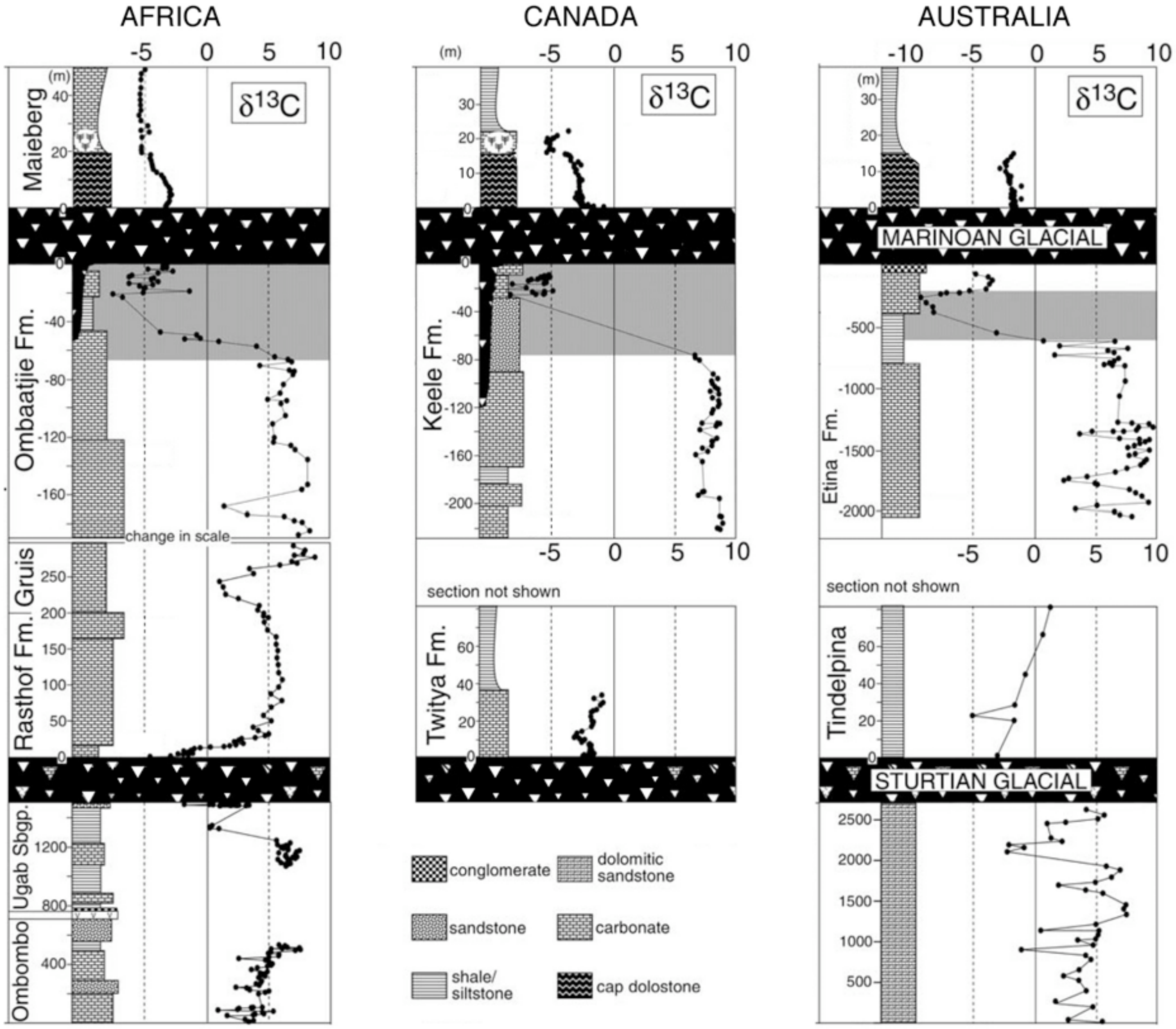


Figure 5-4. Detailed carbon isotope records for Neoproterozoic sections from three continents (Halverson et al., 2005). The Marinoan glaciation was centered at about 650 million years ago and the Sturtian glaciation at about 720 million years ago. Also shown are lithologies and local names for the stratigraphic units.

the extent of alteration. It is based on a Neoproterozoic section exposed in Mongolia. Unlike the other sections which are dominated by dolomite, this one is entirely limestone. A comparison of their results with those from other sections reveals that the dolomite $\delta^{13}C$ values were often shifted toward values associated with the Phanerozoic marine carbonates (i.e., toward $\delta^{13}C \sim 0$). In other words, highly positive $\delta^{13}C$ values were lowered and highly negative $\delta^{13}C$ values were raised. While these shifts were in some cases large, in others, they were quite small or nonexistent. Presumably they were the result of isotopic replacement during dolomitization.

Another consideration is that the carbon isotope values likely represent steady states rather than transients. The reason is that unless the residence time of DIC in the ocean was much larger than today's (i.e., ~10^5yrs), the time elapsed between sampling points was long compared to the residence time. If this is the case, then isotopic composition of the carbon buried in sediments must match that for the input. If, as is generally accepted, the input has a $\delta^{13}C$ of about -5 per mil, then depending on the positioning of carbon between organic matter and carbonates, the $\delta^{13}C$ for limestone must lie within the range -5 to +20 per mil (see Fig. 5-5).

As summarized in Figure 5-5, the $\delta^{13}C$ for the limestone (and for some of the dolomites) for the multi-million-year time intervals separating the low ^{13}C events range from +6 to +10 per mil assuming that the carbon added to the ocean-atmosphere reservoir has a $\delta^{13}C$ of -5 per mil and that the $\delta^{13}C$ of the organic matter buried in sediments is on the average 25 per mil lower than that for marine carbonate, then these ambient values correspond to fractions of organic matter contribution to the burial of carbon of 40 to 60 percent.

Except for the Wonoka excursion (see below), the $\delta^{13}C$ drops associated with the snowball events bottom out in the range -5 to -6 per mil. This corresponds to what would be expected if the carbon added to the ocean-atmosphere reservoir were precipitated entirely as carbonate. It should be noted that $\delta^{13}C$ values lower than -6 per mil cannot be explained by this scenario.

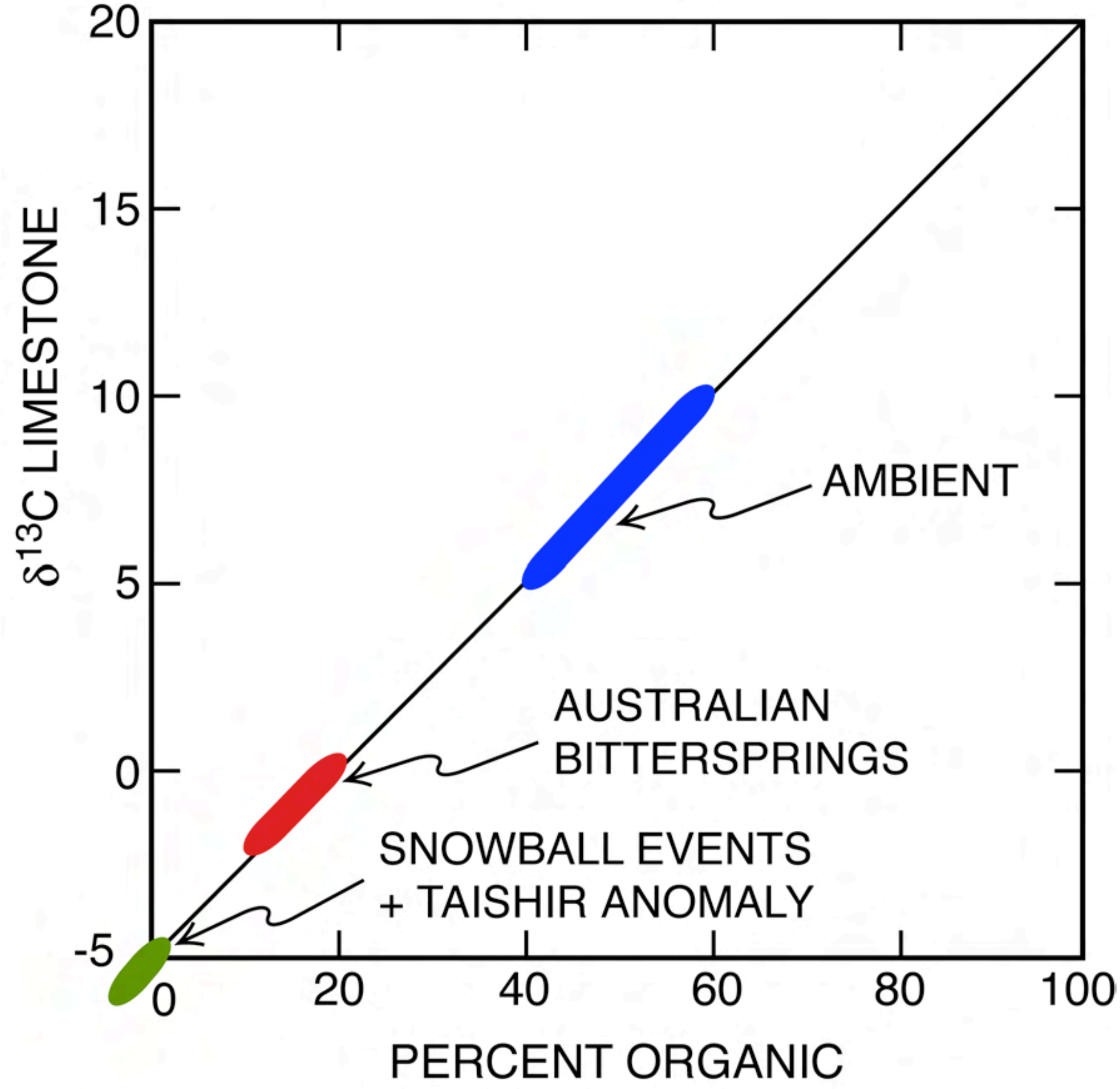


Figure 5-5. Assuming that the variations in δ^{13}C of Neoproterozoic carbonates represents primarily the steady-state partitioning of carbon buried in marine sediments between organic matter and $CaCO_3$, this graph shows the fraction of organic matter deposited during the ambient conditions separating the dips during the Bitter Springs dip and during the Snowball and Taishir event.

The Bitter Springs $\delta^{13}C$ decline (see Fig. 5-6) plateaued at a value of -0.1 ± 0.2 per mil suggesting that the fraction of carbon buried as organic matter dropped only to about 20 percent and never went to zero.

During the Taishir anomaly (see Fig. 5-7) which took place halfway between the two major snowball events (i.e., at about 655 million years ago), the $\delta^{13}C$ underwent a sharp decline to about -6 per mil and then turned around and went back up to about +9 per mil. There is no evidence of a freeze-up. Hence, the termination of this episode could not be the result of a large CO_2 buildup.

There is one additional carbon isotope excursion, the Wonoka anomaly (see Fig. 5-8). It is the last of the series coming just before the onset of the Cambrian. It differs from the others in that the $\delta^{13}C$ drops to -10 per mil, a value excluded if partitioning between $CaCO_3$ and organic matter were the sole cause. As this drop to -10 per mil is recorded on three separate continents (Fig. 5-8), it must be real and it must be global. As such a drop cannot be explained by any mixture of organic and carbonate produced by the throughput of carbon with a composition of -5 per mil, it undermines the obvious interpretation of the carbon isotope data set for the Neoproterozoic.

So what caused these $\delta^{13}C$ drops? One possibility is that the CO_2 content of the atmosphere dropped below that level where photosynthetic organisms could function. Presumably the oceans $CO_3^{=}$ x Ca product then rose until an extent of supersaturation permitted $CaCO_3$ to precipitate was achieved. In some cases the CO_2 drawdown culminated in earth freeze-ups which would terminate $CaCO_3$ formation and allow the CO_2 released by planetary degassing to accumulate. This would continue until the consequent greenhouse warming led to a thaw. But something else must have terminated the Bitter Springs and Taishir declines, for in neither case is there evidence for a global freeze-up. In the case of the Bitter Springs, the decline leveled out and there was a several million-year plateau during which deposition of organic matter must have continued. This plateau came to an abrupt end and the $\delta^{13}C$ of limestone returned to its

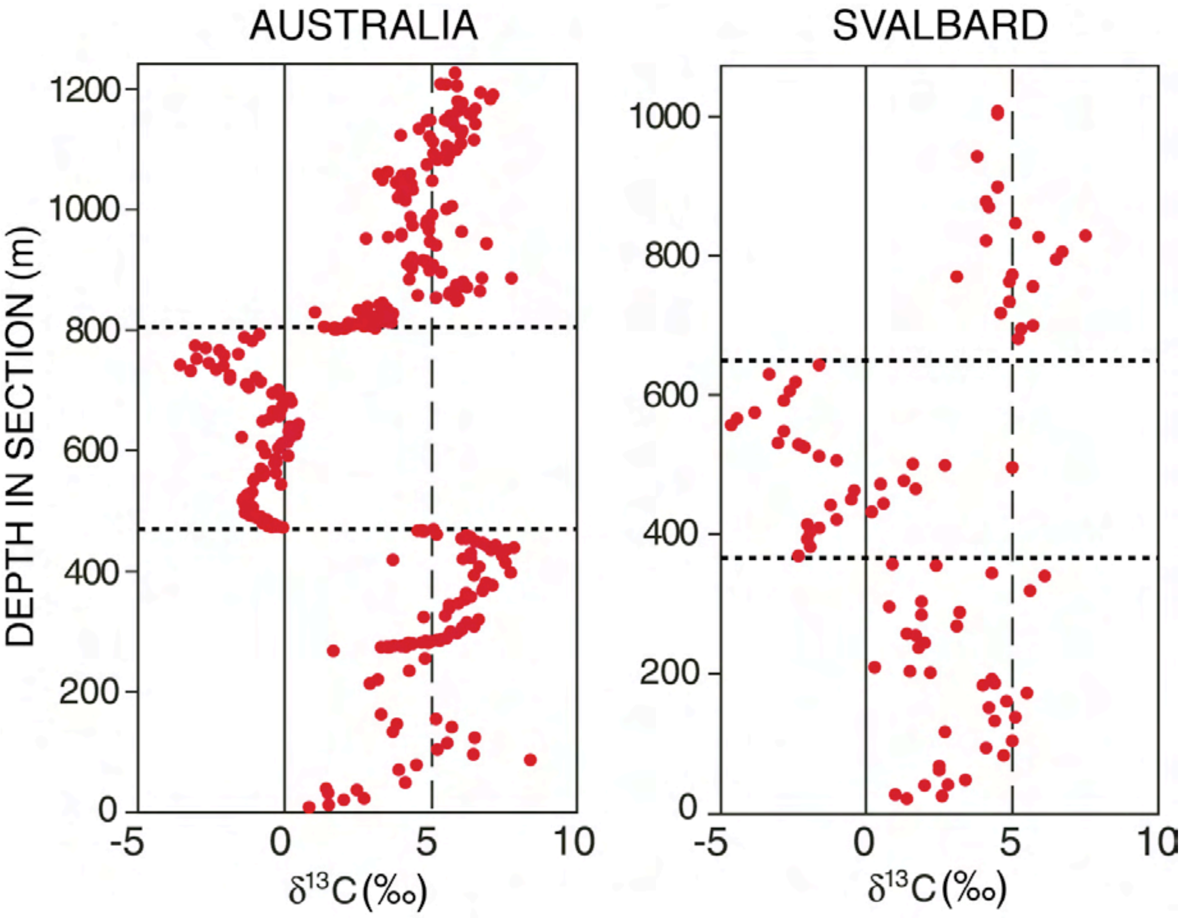


Figure 5-6. Carbon isotope records for Bitter Springs formation limestone in Australia and for its equivalent in Svalbard (Halverson et al., 2005). There is no evidence that the Earth froze over during the time of this δ^{13}C minimum. The age of the event is close to 800 million years. It is interesting to note that the oxidation of the element chromium commenced close to this time (see Planavsky et al., 2014). It marks a rise in the atmosphere's CO_2 content.

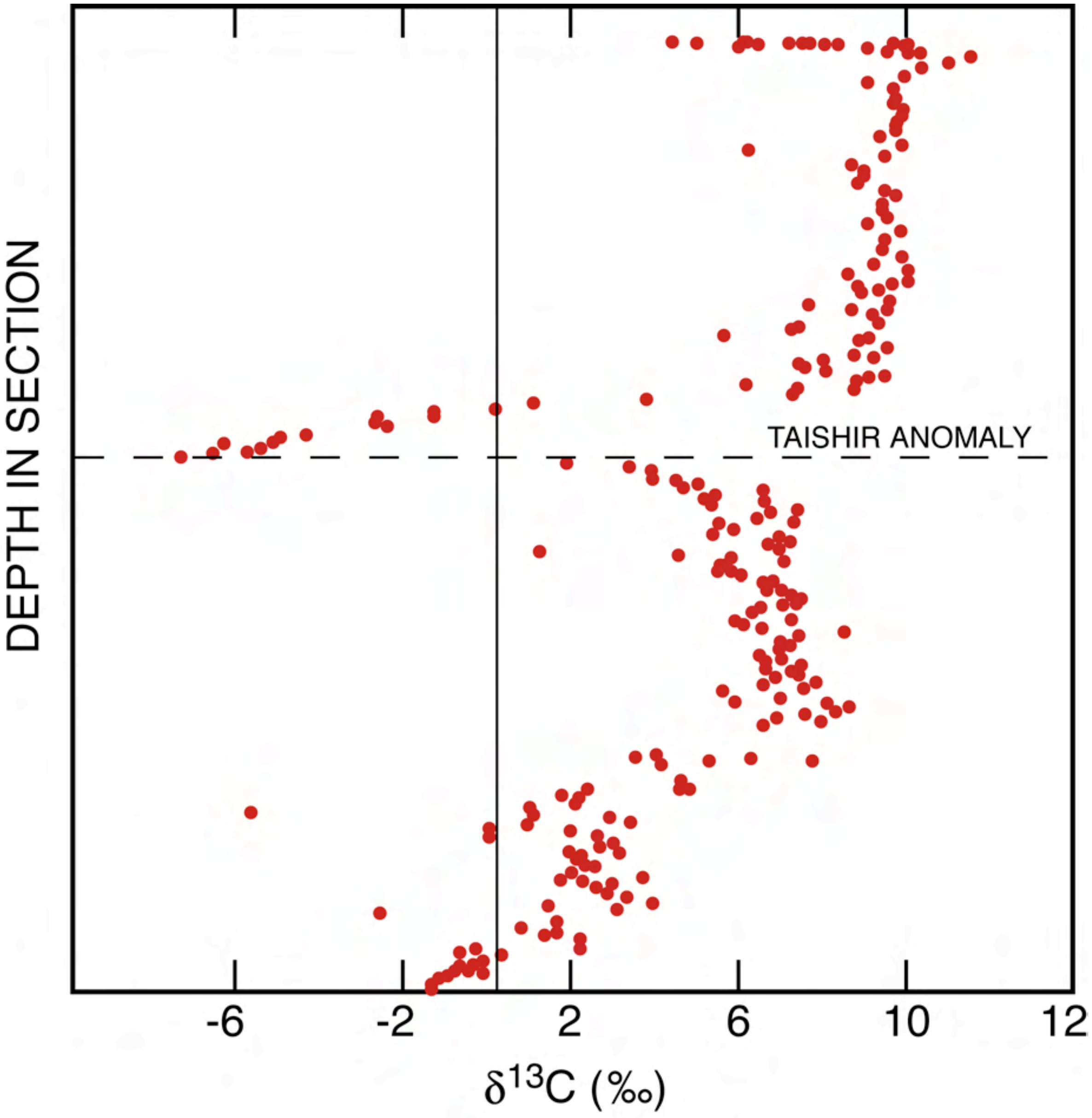


Figure 5-7. The sharp dip in $\delta^{13}C$ of limestone which occurred about halfway between the Sturtian and Marinoan global glaciations (i.e., about 655 million years ago) is referred to as the Taishir anomaly. At its peak, the $\delta^{13}C$ dropped to the level characterizing Snowball events. Yet, there is no evidence for a global glaciation.

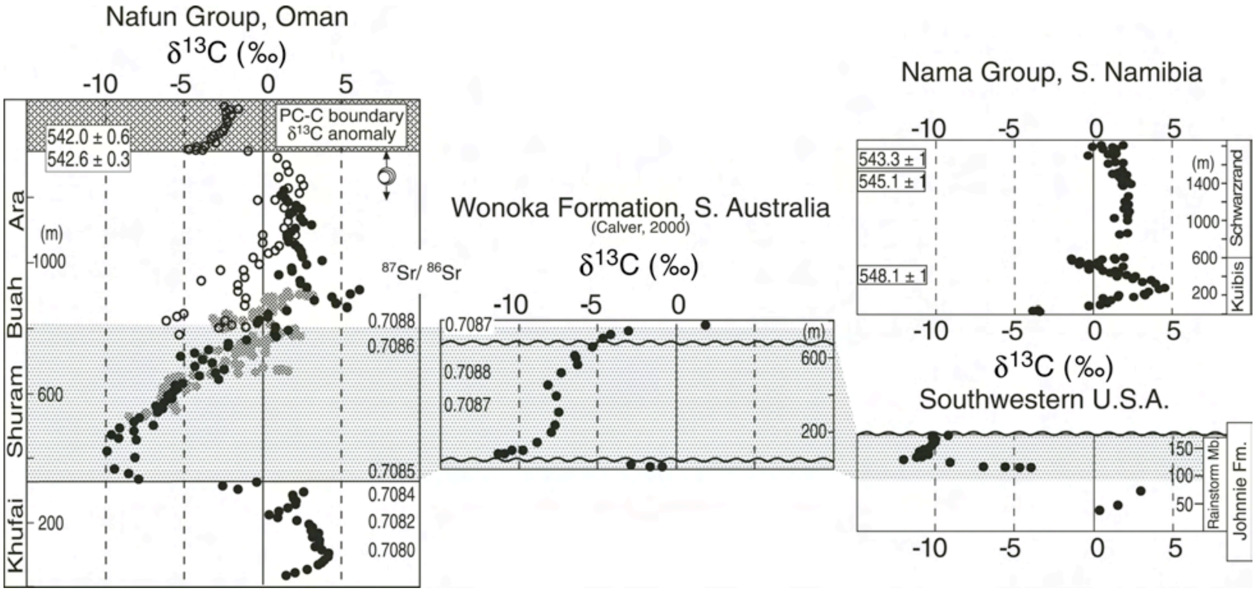


Figure 5-8. Carbon isotope records for the Wonoka anomaly from three different continents (Halverson et al., 2002). The important point to be made is that in each, the $\delta^{13}C$ drops to -10 per mil, well beyond the value of -6 per mil expected if the CO_2 added to the ocean-atmosphere reservoir were removed in the form of $CaCO_3$. Hence something beyond partitioning between $CaCO_3$ and organic residues must have occurred.

ambient value. In the case of Taishir anomaly, no sooner had the $\delta^{13}C$ bottomed out, it began to climb back toward its ambient value.

One way to interpret the drops in ^{13}C would be to propose a runaway greenhouse disaster. If, for some reason, the atmospheric CO_2 content dipped low enough that photosynthetic was crippled, this would not only cut off the production of organic matter but also that of the $CaCO_3$ produced by marine organisms. Calcium would then have been supplied to the ocean faster than it was utilized causing the extent of the $CaCO_3$ supersaturation to increase. If so, a point would have been reached where inorganic precipitation normally blocked by Mg and other ions present in seawater could take place. Were this to have happened, then all the carbon added to the ocean would have been deposited as $CaCO_3$ and its $\delta^{13}C$ would have shifted to the -5 per mil value for planetary outgassing.

Of interest is that timing of the first of these drops in $\delta^{13}C$, i.e., that associated with the Bitter Springs stage (see Fig. 5-6), matches that for first appearance of chromium isotope fractionation (see Fig. 4-3). Perhaps the appearance of multi-celled organisms which took place at about this time played a role in disrupting the flow of carbon through the ocean-atmosphere reservoir.

Although we lack a firm scenario to explain how the Earth's carbon cycle spun off track, it makes sense that it was CO_2 that bailed us out. Once frozen, the surface Earth carbon cycle, as we know it, would have been shut down. There would have been no soils, no rivers and no ocean. But, as the Earth's interior would have been unaware of the disaster occurring at its surface, the great crustal plates would have continued to move. Hot magma would have been pushed up at spreading centers. Subduction would have continued to feed arc volcanoes. Some of the CO_2 released from these magmas would have found its way through the ice into the atmosphere. But it would not have been deposited as $CaCO_3$ nor as organic matter. Hence, the CO_2 concentration in the atmosphere would have become ever larger. At some point, the greenhouse impact of the extra CO_2 would become great enough to more than compensate for the sunlight reflected off the planet's icy surface. Melting would have begun. As land and water reappeared, the Earth's reflectivity would have been steadily reduced. Eventually the ice would have disappeared altogether and the Earth would have gone from being very cold to very hot. Hot because in the absence of reflective ice, all that extra CO_2 would have made Earth a hothouse. It is surprising that life survived this double whammy. Those organisms that weren't done in by the freeze-up had to survive temperatures which were likely high enough to wipe out their biochemical apparatus.

The thaw would have allowed the supply of calcium to the ocean not only to have resumed but its rate would have been far higher than before the freeze-up. On a hot Earth bathed in rains made very acid by atmosphere's high CO_2 content, the rate of weathering must have been much greater than now. Given Ca to mate with, the reservoir of extra atmospheric CO_2 would have been steadily drawn down. As the CO_2 must have had a whole Earth carbon isotopic composition (i.e.-5‰) so also would the limestone. Further, as the rate of $CaCO_3$ burial would have been far faster than the rate of organic burial, nearly all the CO_2 must have been converted to $CaCO_3$.

This all sounds very logical, but there is a serious flaw. Both the Bitter Springs and the Taishir $\delta^{13}C$ drops culminated in the absence of a snowball episode. This being the case, if CO_2 was the savior, then some other scenario would have to be proposed to explain its buildup.

Although much more must be learned, it appears that CO_2 played both the role of villain and of savior. A drop in CO_2 likely triggered the freeze-up and a buildup of CO_2 was responsible for the thaw. But it must be emphasized that the scenario presented here is only one of several on the table. Further, there are those who believe that the dips in $\delta^{13}C$ are hopelessly diagenetic. If this is the case, then our main source of information regarding the cause of these freeze-ups would be lost. To me, the consistency of the $\delta^{13}C$ results both stratigraphically at one locale and geographically at several locales argues against dominance of diagenesis. It has something very important to tell us. But, as yet we are not sure what it is.

References for Chapter 5

Calver, C. R. (1998), Isotope stratigraphy of the Neoproterozoic Togari Group, Tasmania, *Australian Journal of Earth Sciences*, *45*, 865-874.

Calver, C. R. (2000), Isotope stratigraphy of the Ediacarian (Neoproterozoic III) of the Adelaide Rift Complex, Australia, and the overprint of water column stratification, *Precambrian Research, 100*, 121-150.

Cozzi, A., P. A. Allen, and J. P. Grotzinger (2004), Understanding carbonate ramp dynamics using δ^{13}C profiles: examples from the Neoproterozoic Buah Formation of Oman, Terra Nova, 16, 62-67. doi: 10.1111/j.1365-3121.2004.00528.x.

Grotzinger, J. P., S. A. Bowring, B. Z. Saylor, and A. J. Kaufman (1995), Biostratigraphv and geochronologic constraints on early animal evolution, *Science 270*, 598-604.

Halverson, G. P., P. F. Hoffman, D. P. Schrag, and A. C. Maloof (2005), Toward a Neoproterozoic composite carbon-isotope record, *GSA Bulletin*, *117*(9/10), 1181-1207, doi: 10.1130/B25630.1.

Halverson, G. P., B. P. Wade, M. T. Hurtgen, and K. M. Barovich (2010), Neoproterozoic chemostratigraphy, *Precambrian Research, 182*, 337-350, doi: 10.1016/j.precamres.2010.04.007.

Hoffman, P. F., and D. P. Schrag (2002), The snowball Earth hypothesis: testing the limits of global change, *Terra Nova*, *14*, 129-155.

Hoffman, P. F., A. J. Kaufman, G. P. Halverson, and G. P. Schrag (1998), A Neoproterozoic snowball Earth, *Science*, *281,* 1342-1346.

Planavsky, N. J., C. T. Reinhard, X. Wang, D. Thomson, P. McGoldrick, R. H. Rainbird, T. Johnson, W. W. Fischer, and T. W. Lyons (2014), Low Mid-Proterozoic atmospheric oxygen levels and the delayed rise of animals, *Science, 346*, 635-638.

Schrag, D. P., R. A. Berner, P. F. Hoffman, and G. P. Halverson (2002), On the initiation of a snowball Earth, *Geochem, Geophys. Geosyst., 3*(6), doi: 10.1029/2001GC000219.

Chapter 6

Basalt Floods

Perhaps the most interesting climate-related volcanic phenomena involves what's referred to as mantle plumes. They are thought to originate at the core-mantle boundary and push their way up through the entire mantle. When they make it to the surface, they erupt producing huge outpourings of basaltic lava. These so-called flood basalts are found at many places including Russia (the Siberian), India (the Deccan), and in North America (the Columbia River). They impact climate in two ways. One is associated with the eruption itself for the magmas contain CO_2, SO_2 and other gases. Their release to the atmosphere alters both its transparency and its greenhouse power and hence climate. Some combination of toxicity and extreme warming might be responsible for the extinctions associated with these outbursts of lava. The other consequence takes place during the aftermath of these eruptions. As basalts undergo chemical weathering at a rate on order of magnitude faster than that for other rocks, flood basalts increase the supply of calcium and, in so doing, tend to cool the Earth by driving down the atmosphere's CO_2 (see Chapter 2). As pointed out by Kent and Muttoni (2013), their impact on calcium release depends on their location on the planet. Within the warm, rainy, highly-vegetated tropics, they erode even faster.

The largest of these outbursts took place in northern Asia 250 million years ago. It covered an area the size of the European continent with a six-to-ten-kilometer-thick sequence of ignimbrites and lava flows. As documented by numerous highly precise uranium, lead ages on zircons contained in volcanic ash layers obtained by Sam Bowring's group at MIT, at this same time, life took an awesome hit. All but 10 or 15 percent of the species then extant were no more. This event marks the end of the Paleozoic era and the onset of the Mesozoic era. Not only did this catastrophe make way for a new cast of animals and plants, but also, a new food web. The age of reptiles was ushered in. Although dinosaurs ruled the roost, organisms far down the food chain controlled the flow of carbon and sulfur through the system. The isotopic record of ^{13}C in $CaCO_3$ and of ^{34}S in $CaSO_4$ tells us that the flow must have been quite different during the Triassic than during the Permian.

Some have proposed that these immense outpourings of lava were triggered by the impact of an extraterrestrial object. The finding that the extinctions associated with the K-T boundary (69 million years ago) occurred at close to the time of both an asteroid hit and an outpouring of a flood basalt (India's Deccan) raises the possibility that the mantle plumes responsible for these great outpourings were launched through the crust by impacts of extraterrestrial objects. But, this was not the case for the Deccan Plume. The magnetic reversal record makes it clear that the flood basalt eruption began before the impact and before the extinctions. There is, however, evidence that the rate of the volcanic eruptions was greater after the impact than before. The only evidence an impact might have triggered the Siberian outpouring is a 40 km diameter crater in central Brazil. Its age of 255 ± 3 million years lies within the uncertainty of the 251 million year age for the Siberian flood basalts. However, it is far, far smaller than the crater produced by the K-T boundary impact (180 km in diameter). Thus it is highly doubtful that it could be responsible for the massive extinctions. An early claim for the presence of extraterrestrial Bucky Balls (soccer-ball-shaped carbon molecules formed in outer space), has subsequently been discredited. So, the focus of thinking regarding the kill has been on gases contained in the basaltic magma. The observation that $CaCO_3$-producing marine benthic organisms took a huge hit while their 'naked' brothers largely survived points to CO_2 as the villain. So also does an 8°C warming recorded by the oxygen isotopic composition of marine $CaCO_3$. If CO_2 was the villain, then rather than playing the role of savior as was likely the case for snowball episodes, it played the role of assassin, snuffing out nearly all life forms.

MIT's Sam Bowring produced an extremely detailed ^{13}C record for the P-T boundary (Fig. 6-1). He documented two ^{13}C spikes of 10^5 years duration which reached -5 and -6 per mil respectively. One explanation would be that these peaks represent times when both ocean and atmosphere carbon was dominated by mantle- derived CO_2 released as the

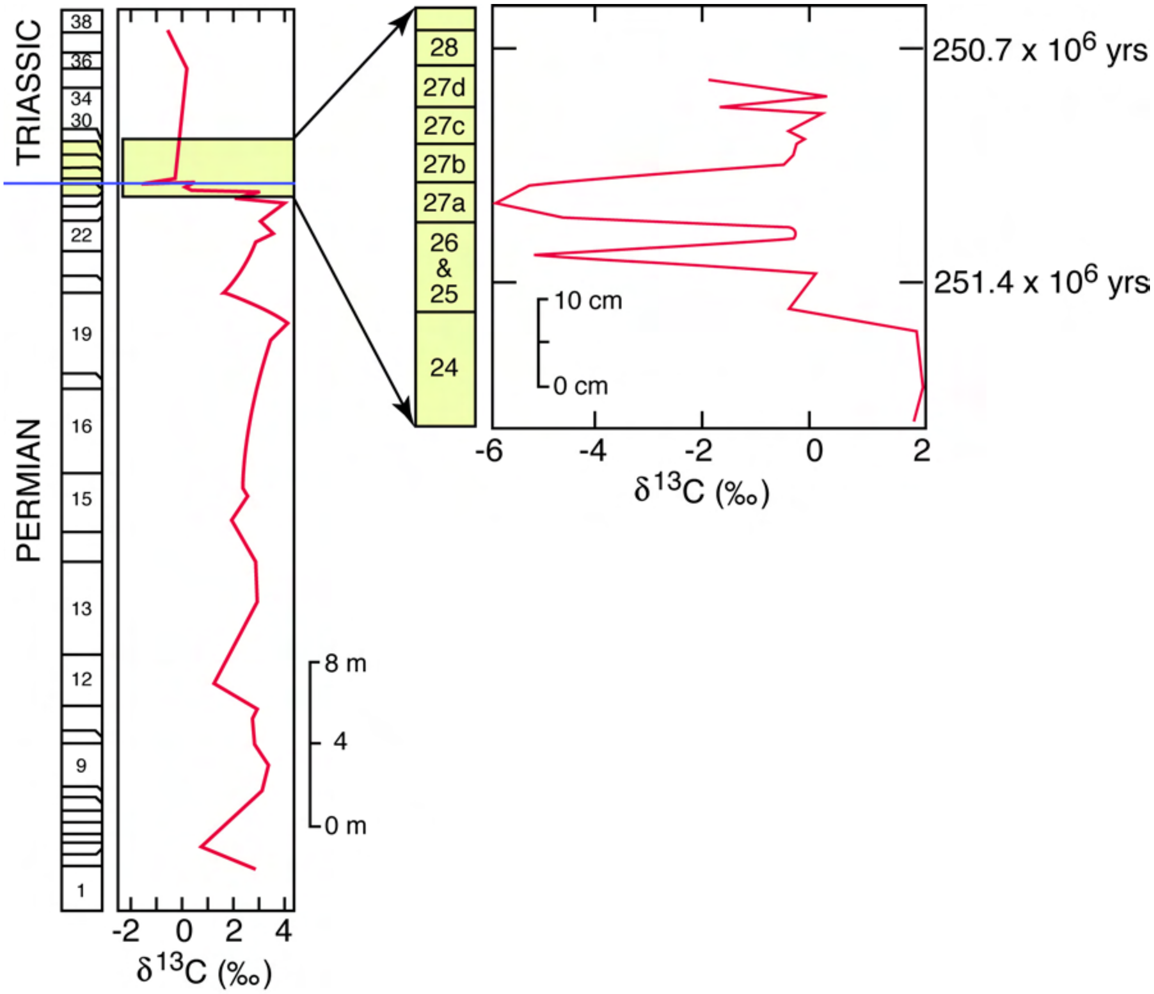


Figure 6-1. A high resolution carbon isotope record for a section spanning the Permian-Triassic boundary near Meishan, China. As is the case for other sections, there is a ~3 per mil shift (+3 to 0‰). However, right at the boundary two negative spikes reaching between -5 and -6 per mil are seen. One interpretation would be that during these short time intervals, the atmospheric CO_2 was dominated by CO_2 released by the massive outpouring of basaltic magma. If so, the CO_2 content of the atmosphere must have been far higher than today's. The very precise uranium-lead ages were obtained on zircons contained in ash beds (Bowring et al., 1998).

result of the flood basalt eruptions. As shown by precise dating of zircons in thin ash layers present in this Chinese sedimentary section, the 251-million-year age of this $\delta^{13}C$ peak nicely matches that obtained for the flood basalts.

Following this initial ^{13}C spike was a longer term downward three per mil shift. It is documented by a number of carbon isotope records spanning the PT boundary (Fig. 6-2). Assuming that the $\delta^{13}C$ of carbon added to the ocean was close to -5 per mil in both the Permian and Triassic, this drop in ^{13}C represents a shift from about 30 percent of the carbon being deposited as organic residues in the late Permian to about 20 percent in the early Triassic.

Many years ago, Holser and Kaplan performed sulfur isotope analyses on all available marine evaporite deposits. Included were 45 evaporites of Permian age which yielded an average $\delta^{34}S$ of 10.5 ± 1.0‰. They were not able to find any evaporates of Triassic age. But there are two Jurassic in age. Both yielded $\delta^{34}S$ values of 14.4‰. Although incomplete, the record suggests that the $\delta^{34}S$ of ocean sulfate underwent a 4 per mil $\delta^{34}S$ increase from Permian to Triassic.

One might ask why there are no more recent results. My guess is that Holser and Kaplan analyzed samples from all the known evaporites. The only additional results of value are those by Stanford's Adina Paytan. She obtained a highly precise record for marine barite but only for the last 120 million years. Currently sulfur isotope analyses are being made on $CaSO_4$ associated with marine $CaCO_3$.

It is interesting to speculate on what a three per mil rise in $\delta^{13}C$ and a four per mil drop in $\delta^{34}S$ might be telling us. Assuming: 1) that the isotopic composition of the sulfur added to the ocean was +8 per mil during both the late Permian and early Triassic, 2) that the fractionation during the reduction of $SO_4^{=}$ to $S^{=}$ averaged -40 per mil, then the fraction of the sulfur deposited in reduced form must have shifted from about 10 percent during the late Permian to 25 percent during the early Triassic (Fig. 6-3). This change in the ratio of carbon to sulfur deposited in reduced form can be quantified if the additional assumption is made that the

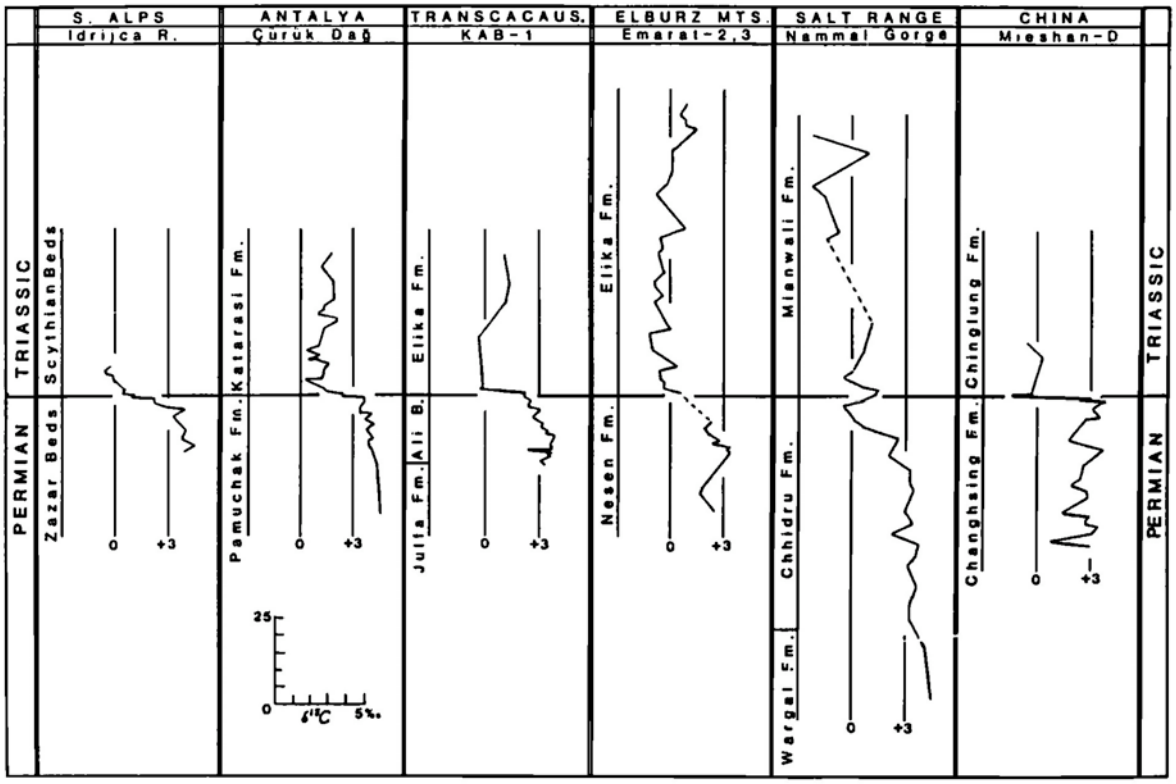


Figure 6-2. Carbon isotope shifts across the Permian-Triassic boundary as recorded in marine carbonates from six different places (summary by Baud et al., 1989).

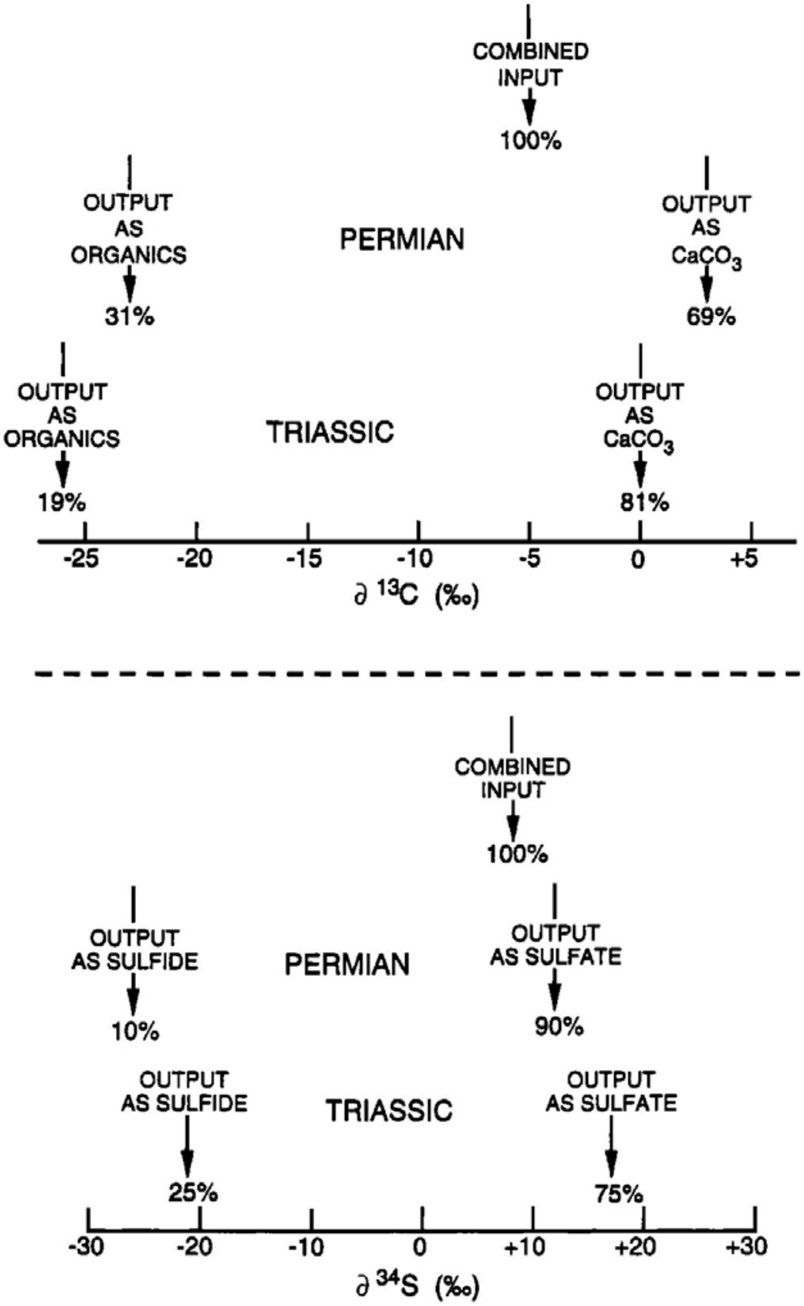


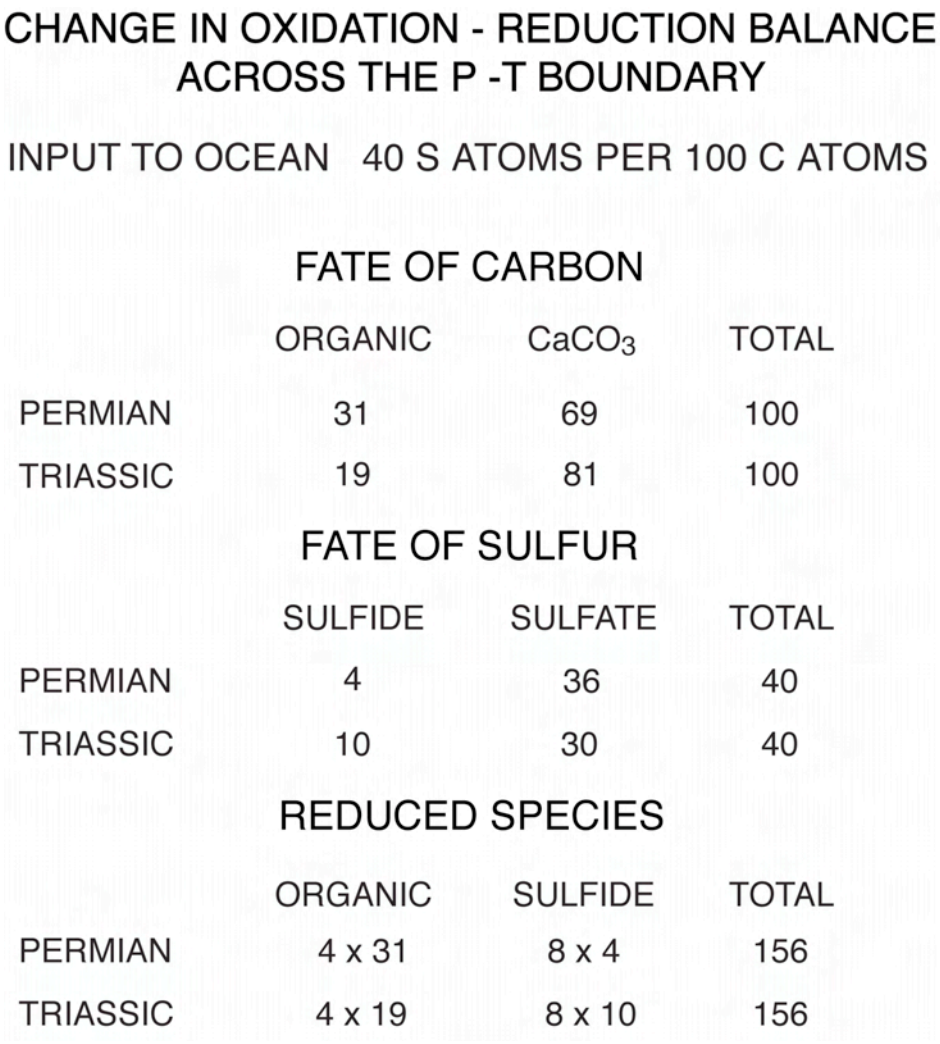
Figure 6-3. Based on the 3 per mil reduction in the δ^{13}C for marine limestone, it appears that the fraction of carbon leaving the ocean shifted from 31 percent in the late Permian to 19 percent in the early Triassic. At the same time, the 6 per mil increase in δ^{34}S suggest an increase in the fraction stored in reduced form from 10 to 25 percent (see Broecker and Peacock, 1999).

oxidation state of the material added to the ocean by chemical erosion and by volcanic emissions was the same in the Triassic as it was in the Permian. Were this the case, then in order to explain both the isotopic shifts and to conserve electrons, the ratio of carbon atoms added to the ocean to sulfur atoms added to the ocean must have been about 2.5 (i.e., 100 C atoms/40 S atoms) (Fig. 6-4).

Although the numerous assumptions adopted for this calculation are quite shaky, the conclusion that reduced sulfur played a more important role in the Triassic than in the Permian is likely correct. If so, one might ask why it happened. Part of the answer is that the lush woody vegetation of the Permian took a large hit during the extinction episode. If so, the amount of organic matter buried on the continents as peat and coal was smaller during the Triassic than during the Permian. Another part of the answer is that large portions of the sea floor appears to have been anoxic during the early Triassic. Such an increase in anoxia would have led to an increased accumulation of sulfides. In thinking about this, it should be kept in mind that continental waters contain so little dissolved SO_4 that there can be no significant sulfate reduction.

Fifty million years later at the end of the Triassic, another massive outflow of basaltic magma took place. A mega-continent which included the Americas, Eurasia and Africa split apart creating what would become the Atlantic Ocean (Fig. 6-5). This rupture was accompanied by eruptions of basaltic magma extending from Newfoundland to Georgia. Precise zircon dating has shown that these eruptions were nearly synchronous taking place over a 0.7 million-year time interval 201 million years ago.

We know that today's basaltic magmas contain gases rich in CO_2. Basalts dredged from the oceanic ridge crests have bubbles filled with this gas. They are known as popping rocks for some of the bubbles 'explode' on the deck of the ship. The reason is that the bubbles formed under a pressure of about 250 atmospheres (i.e., at about 2500 meters depth). When this pressure is released, some of the bubbles rupture releasing the trapped gas. Carbon isotope measurements on the CO_2 contained in these bubbles is one of the chief ways that



CHANGE IN OXIDATION - REDUCTION BALANCE
ACROSS THE P -T BOUNDARY

INPUT TO OCEAN   40 S ATOMS PER 100 C ATOMS

FATE OF CARBON

	ORGANIC	$CaCO_3$	TOTAL
PERMIAN	31	69	100
TRIASSIC	19	81	100

FATE OF SULFUR

	SULFIDE	SULFATE	TOTAL
PERMIAN	4	36	40
TRIASSIC	10	30	40

REDUCED SPECIES

	ORGANIC	SULFIDE	TOTAL
PERMIAN	4 x 31	8 x 4	156
TRIASSIC	4 x 19	8 x 10	156

Figure 6-4. One way to explain the opposing changes in the isotopic compositions of marine limestone (^{13}C) and marine gypsum (^{34}S) across the Permo-Triassic boundary is to call on a decrease in the burial of reduced carbon and an increase in the burial of reduced sulfur. If the chemical composition of the inputs and the isotope fractionation between the oxidized and reduced forms of S and C remained unchanged, then electron conservation requires that for every 100 carbon atoms added to the ocean, there were 40 sulfur atoms. It must be kept in mind that although 4 electrons are involved in the reduction of carbon, 8 are involved in the reduction of sulfur.

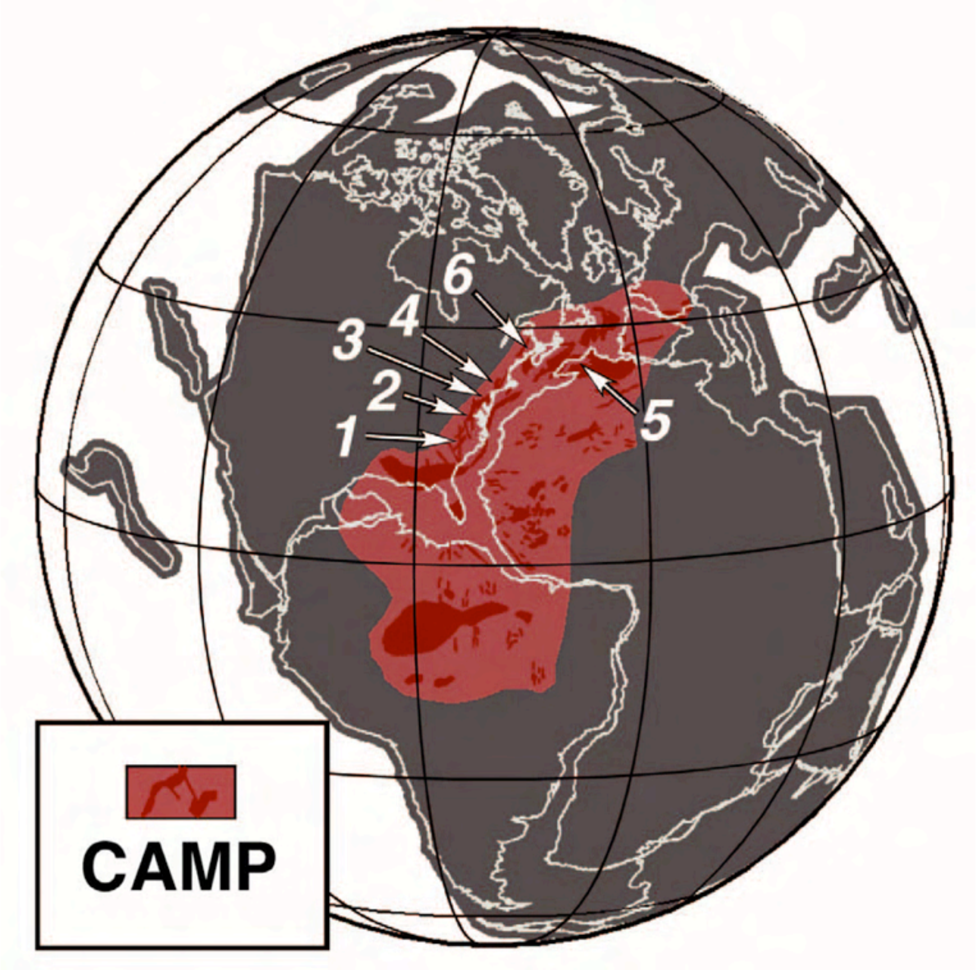


Figure 6-5. Map showing the breakup of the supercontinent Pangea. About 20 million years after the breakup commenced, massive basalt eruptions occurred during a brief interval (0.6 Ma) centered at 201 million years ago. Remnants of these basalts are found along the east coast of North America and in North Africa (Blackburn et al., 2013). They are referred to as the Central Atlantic Magmatic Province (i.e., CAMP).

the -5 per mil $\delta^{13}C$ for the carbon in the Earth's interior has been established.

Morgan Schaller, Jim Wright and Dennis Kent of Rutgers University carried out a study designed to determine whether these massive basalt eruptions released enough CO_2 to raise the atmospheric content. To do this, they employed Cerling's soil $CaCO_3$ method. They did this by comparing the carbon isotope composition of carbonate nodules in soils from just above and just below the series of basalt flows (Fig. 6-6). What they showed is that $CaCO_3$ nodules from soils above the series of flows were less ^{13}C depleted than those from below the basalts (Fig. 6-7). Assuming that the respiration contribution to the soil CO_2 was 3000 μatm, they calculated the atmospheric CO_2 partial pressure at the time the $CaCO_3$ nodules formed. Based on these results, they concluded that the atmospheric CO_2 content before the eruptions hovered about 2000 ppm and after the last of the eruptions, it rose to about 5000 ppm.

Although they make a reasonably strong case that the CO_2 content of the atmosphere was higher after the eruptions than before, their choice of 3000 μatm as the respiration contribution is in my estimation arbitrary. They would have been on firmer ground had they calculated the fractional increase in CO_2 caused by the eruptions for it is independent of the choice of the respiration contribution. Further, it would have been safer to assume that the soil temperature did not change significantly than to assign one. As shown in Figure 6-8, the increase in CO_2 depends strongly on the soil CO_2 concentration. But, as can be seen, that for any choice of the respiration pCO_2, in order to explain the $\delta^{13}C$ increase of 2.2 ± 0.8 per mil, there must have been an increase in atmospheric CO_2 content. But, it could have been anywhere in the range from 1000 μatm to 5000 μatm.

So, there is still much to be learned about the connection between flood basalt outbursts and extinctions. For that 250 million years ago in Siberia, there were massive extinctions but no convincing evidence that it was accompanied by an extraterrestrial impact. However, the ^{13}C record is consistent with a large rise in atmospheric CO_2 content. For that 200 million years ago associated with the opening of the Atlantic, there is also no convincing evidence that it was triggered by an impact. But there were extinctions and the CO_2 content of the atmosphere appears to have undergone a sizable increase. For the 70 million years ago Deccan basalt flood, there was both an impact and extinctions, although the timing of the extinctions matches that of the impact, that of the onset of the basalt flood definitely predates both. This tells us that the tie between impacts, flood basalts and impacts needs much further study.

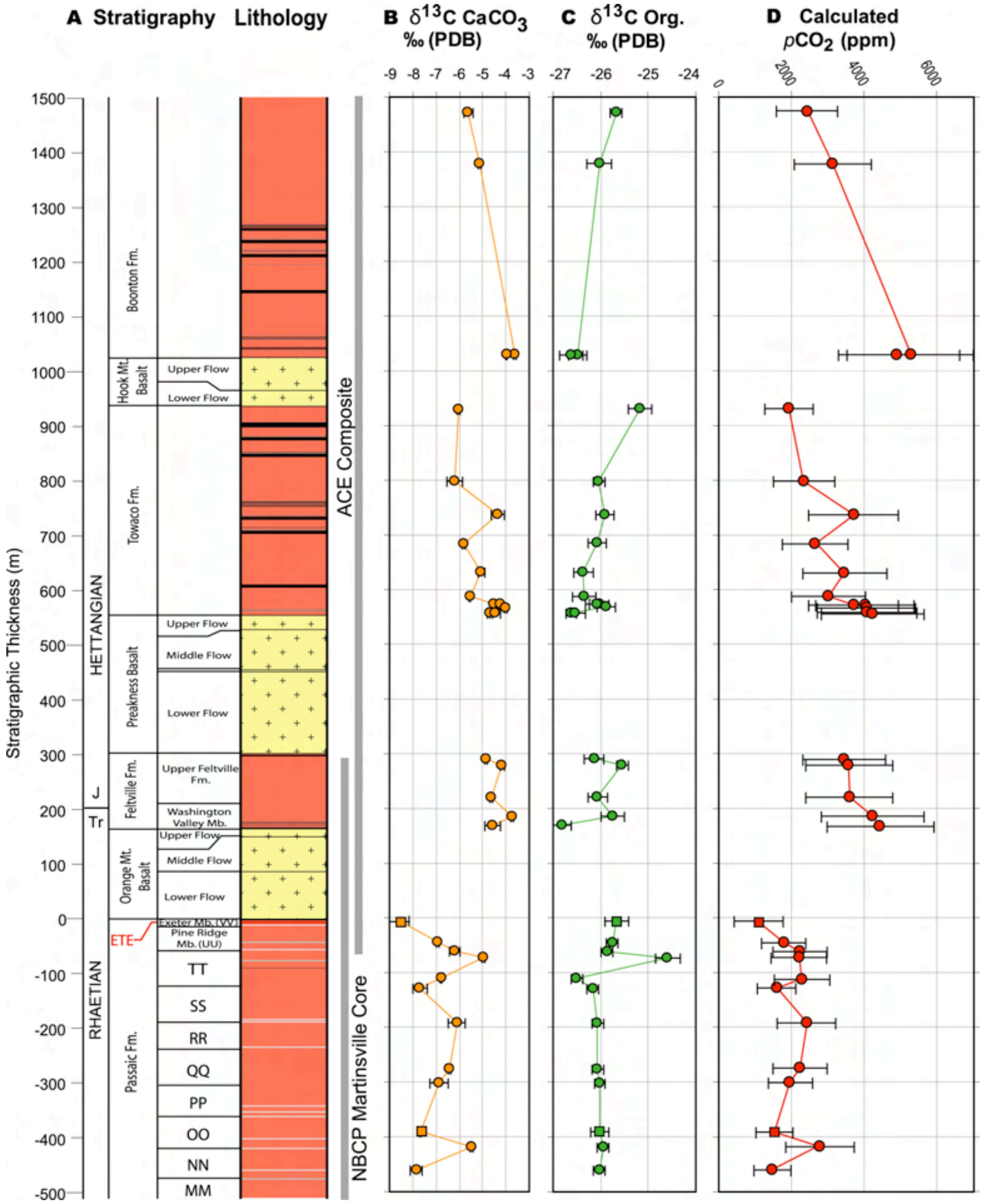


Figure 6-6. Two hundred million years ago a rift developed between Africa and North America. It marked the opening of the Atlantic Ocean Accompanying this opening were massive outpourings of basaltic magmas. In an attempt to determine whether the CO_2 released from these magmas warmed the Earth, Schaller et al. (2011) made carbon isotope measurements on $CaCO_3$ and organics matter contained in paleo soils in four sedimentary horizons: one beneath the basalt sequence, two within it and one above it. As can be seen, the $\delta^{13}C$ for the soil $CaCO_3$ deposited before the onset of the basalt eruptions averaged close to -7 per mil. Those formed immediately after the last of these eruptions had ratio close to -5 per mil. Schaller et al. interpret this 2 per mil shift to a dilution of the respiration CO_2 (~ -26‰) with CO_2 from the atmosphere (~ -6‰). The yellow units are the basalt flows and the red, the sediment and soil between the basalts.

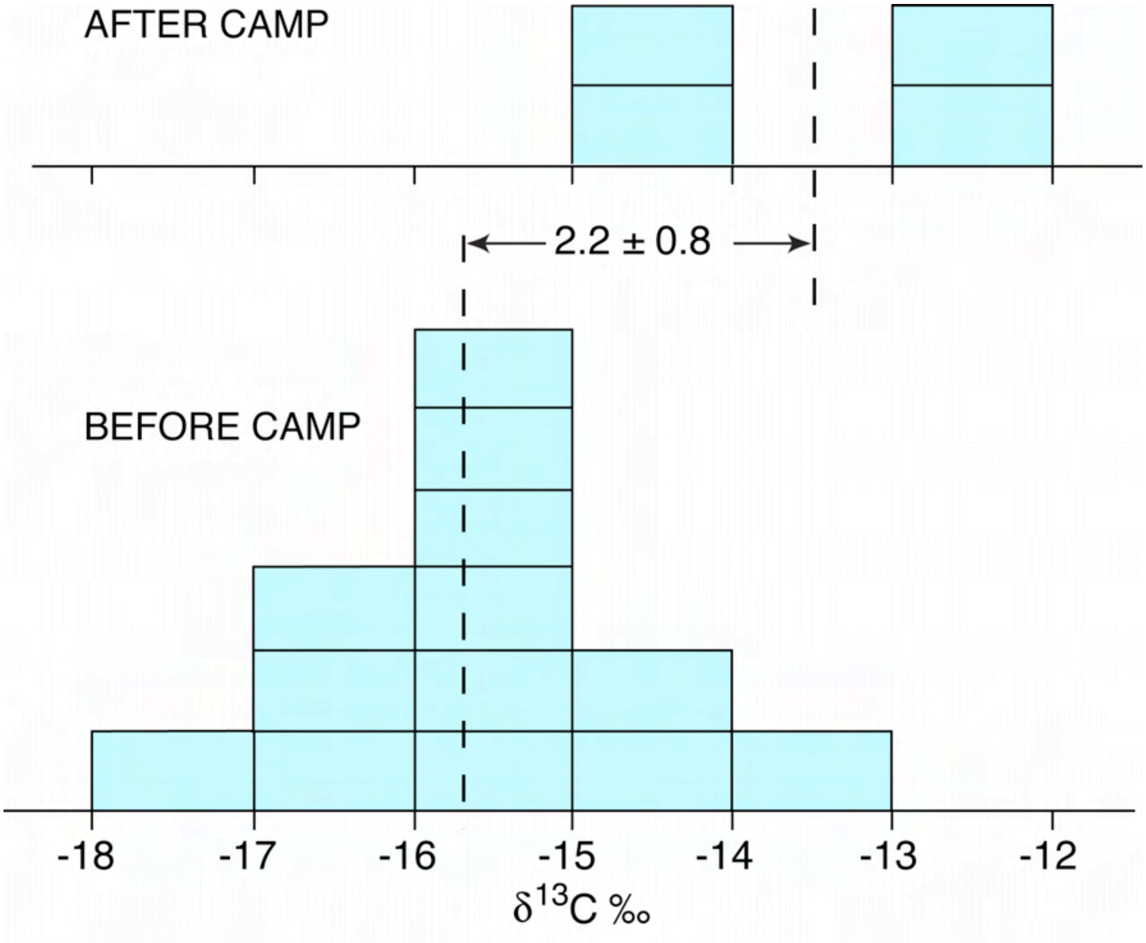


Figure 6-7. Histograms of the $\delta^{13}C$ for soil CO_2 calculated from carbon isotope measurements on soil $CaCO_3$. The lower panel shows those for $CaCO_3$ from pre-CAMP soils (mean -15.7‰) and the upper panel those for past-CAMP soils (mean -13.5‰). The increase of 2.2‰ is consistent with the conclusion that the emission of CO_2 associated with the massive outpouring of basaltic lavas raised the atmosphere's CO_2 content.

$$\Delta p_{CO_2} = \left[\left(\frac{\Delta^{13}\delta C_{SOIL\text{-}RESP.}}{\Delta^{13}\delta C_{AIR\text{-}SOIL}} \right)_{AFTER} - \left(\frac{\Delta^{13}\delta C_{SOIL\text{-}RESP.}}{\Delta^{13}\delta C_{AIR\text{-}SOIL}} \right)_{BEFORE} \right] p^{RESP.}_{CO_2}$$

$$\Delta p_{CO_2} = \left(\frac{12.5}{6.5} - \frac{10.3}{8.7} \right) p^{RESP.}_{CO_2}$$

$$\Delta p_{CO_2} = 0.74 \pm 0.20\ p^{RESP.}_{CO_2}$$

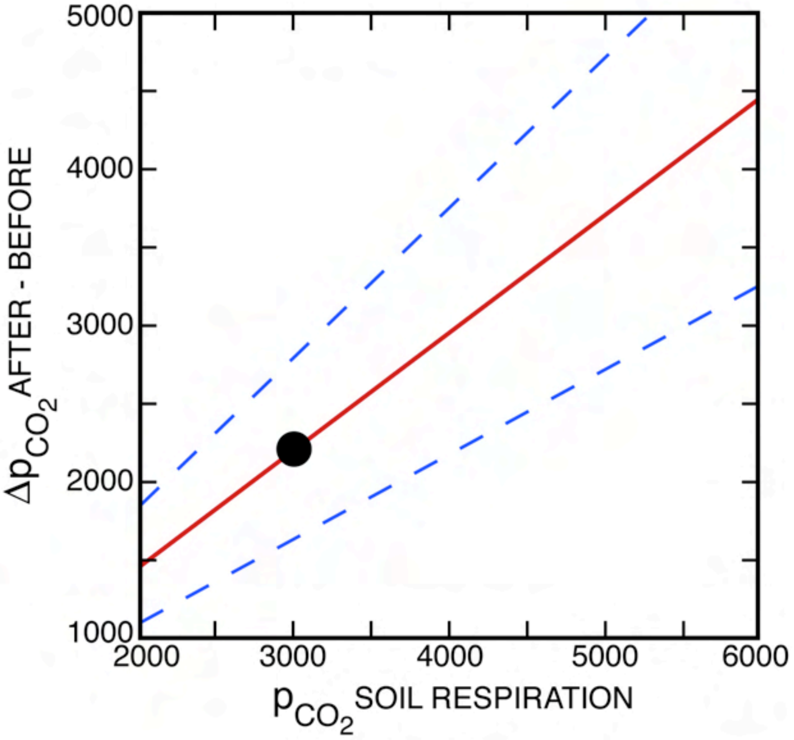


Figure 6-8. The difference in the $\delta^{13}C$ for soil $CaCO_3$'s before and after the CAMP eruptions can be used to constrain the associated increase in atmospheric CO_2 content. However, the result is highly sensitive to the choice of respiration CO_2 content of the soil at the time when the $CaCO_3$ nodules formed. It is also quite sensitive to the uncertainty in the magnitude of the $\delta^{13}C$ shift. The solid line corresponds to the best estimate of $\Delta\delta^{13}C$ $CaCO_3$ (i.e., 0.74). The dashed lines are the limits assuming that the uncertainty in $\Delta\delta^{13}C$is 0.20‰. Schaller et al. made what I consider to be an arbitrary choice of 3000 ppm for the respiration CO_2 content of the soil air (circle).

References for Chapter 6

Baud, A., M. Magaritz, and W. T. Holser (1989), Permian-Triassic of the Tethys: Carbon isotope studies, *Geol. Rundsch. 78*, 659-677.

Blackburn, T. J., P. E. Olsen, S. A. Bowring, N. M. McLean, D. V. Kent, J. Puffer, G. McHone, E. T. Rasbury, and M. Et-Touhami (2013), Zircon U-Pb geochronology links the end-Triassic extinction with the central Atlantic magmatic province, *Science, 340*, 941-945.

Bowring, A. A., D. H. Erwin, Y. G. Jin, M. W. Martin, K. Davidek, and W. Wang (1998), U/Pb zircon geochronology and tempo of the end-Permian mass extinction, *Science*, *280*, 1039- 1045.

Broecker, W. S., and S. Peacock (1999), An ecologic explanation for the Permo-Triassic carbon and sulfur isotope shifts, *Global Biogeochem. Cycles, 13*, 1167-1172.

Burgess, S. D., S. Bowring, and S.-z. Shen (2014), High-precision timeline for Earth's most severe extinction, *PNAS*, *111*, 3316-3321.

Kent, D. V., and G. Muttoni (2013), Modulation of Late Cretaceous and Cenozoic climate by variable drawdown of atmospheric $p\mathrm{CO}_2$ from weathering of basaltic provinces on continents drifting through the equatorial humid belt, *Clim. Past, 9*, 525-546.

Magaritz, M., R. Baer, A. Baud, and W. T. Holser (1988), The carbon-isotope shift at the Permian/Triassic boundary in the southern Alps is gradual, *Nature*, *331*, 337-339.

Schaller, M. F., J. D. Wright, and D. V. Kent (2011), Atmospheric P_{CO2} perturbations associated with the central Atlantic magmatic province, *Science*, *331*, 1404-1409.

Tohver, E., C. Lana, P. A. Cawood, I. R. Fletcher, F. Jourdan, S. Sherlock, B. Rasmussen, R. I. F. Trindade, E. Yokoyama, C. R. Souza Filho, and Y. Marangoni, (2012), Geochronological constraints on the age of a permo-Triassic impact event: U-Pb and ^{40}Ar/^{39}Ar results for the 40 km Araguainha structure of central Brazil, *Geochim. et Cosmochim. Acta, 86*, 214-227.

Chapter 7

The PETM Carbon Event

Fifty-five million years ago, several billion tons of carbon in the form of CO_2 were added to the Earth's atmosphere. It temporarily warmed the planet by about 5°C. The event is referred to as the Paleocene-Eocene Thermal Maximum (or for short, the PETM). This discovery involved the study of deep sea sediment cores from a number of places on the planet (Fig. 7-1). Although there is agreement that this warming lasted 50 thousand or so years, a wide range of estimates have been made regarding the time interval over which it was launched. The favored scenario is that the CO_2 was formed from CH_4 released by the decomposition of clathrates stored in continental margin sediments. If so, the release was likely spread over thousands of years. Then, in 2013, Jim Wright and Morgan Schaller of Rutgers University attempted to upset this apple cart based on the analyses of a series of cores deposited in shallow water on New Jersey's coastal plane. They make a case that the release happened in less than a decade. As this book was being written, an animated discussion was in progress between the 'old guard' who had proposed that the source was methane clathrates and the 'new boys on the block' who favored a comet. As it makes an interesting story, let's start from the beginning.

It is rumored that the late Nick Shackleton, famous for his pioneering research on the ^{18}O and ^{13}C records on foraminifera shells from deep sea cores, came close to discovering this event. He measured the ^{18}O to ^{16}O ratio in planktic forams from a deep sea core which penetrated the Paleocene-Eocene boundary. In his otherwise smooth record there was one outlier. But alas, he disregarded it.

Then, in 1991, Jim Kennett of University of California, Santa Barbara led a deep sea drilling expedition in the Southern Ocean. In one of the cores, the now famous ODP 690, he encountered blips in both ^{18}O and ^{13}C located at the Paleocene–Eocene boundary (Fig. 7-2). Rather than passing it off as a flyer, Kennett homed in on it. The ^{18}O dropped abruptly by a little more than one per mil and the ^{13}C dropped by about three per mil. As the fractionation of oxygen isotopes between seawater calcite shells decreases by about 0.2‰ per degree Celsius, the ^{18}O

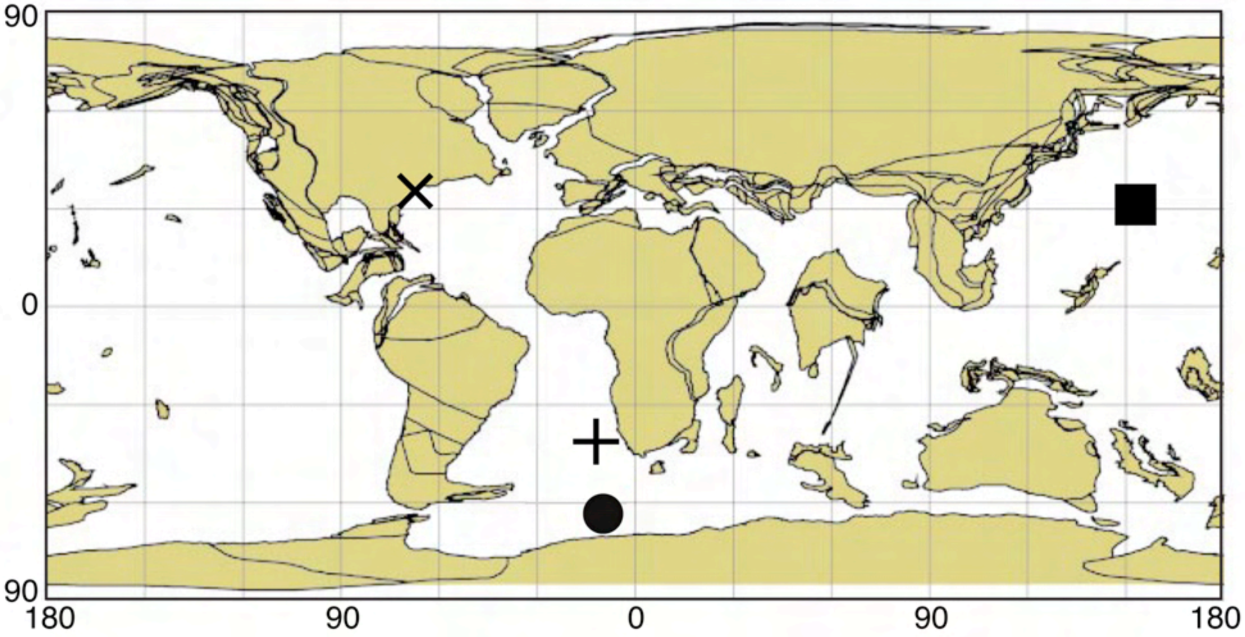


Figure 7-1. Location of the four PETM core sites discussed in this chapter. The circle is for ODP690. The plus is for ODP208 cores. The cross is for the core sediments deposited in shallow waters off the then east coast of North America. The square is for the core on the Shatsky Rise. Note that the positions of the continents shown here are those reconstructed for 55 million years ago rather than todays.

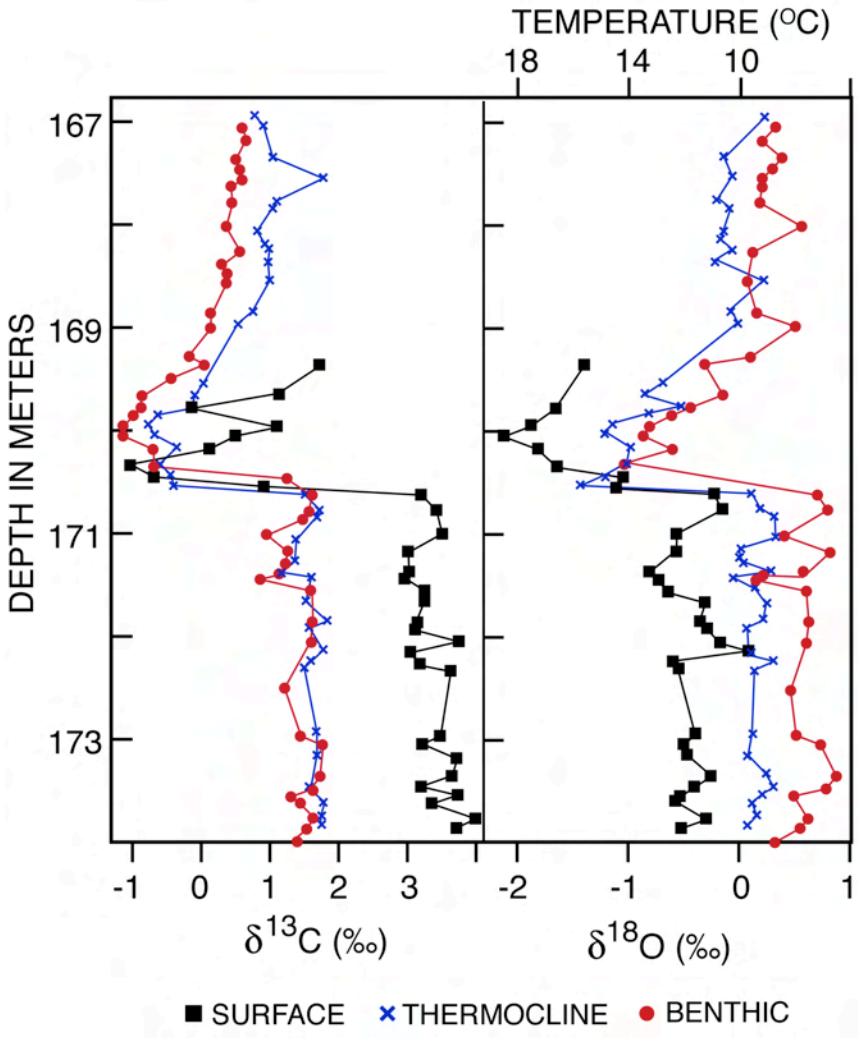


Figure 7-2. As part of the 1989 expedition sponsored by the Ocean Drilling Program (ODP), Jim Kennett chose a site in the Atlantic sector of the Southern Ocean. When he made ^{13}C and ^{18}O analysis of foraminifera shells from this core, he encountered a puzzling anomaly. Both the δ^{13}C and δ^{18}O values underwent abrupt jumps to more negative values. Then over the next 50 or so thousand years, these isotopic compositions returned to the level they had been before the jump. As such an anomaly had never been seen, he puzzled over what it might be telling him. As this bump was present in not only the record for surface dwelling foraminifera but also for those inhabiting intermediate depth and abyssal waters, he concluded that it was likely ocean-wide in extent. The ^{18}O shift corresponded to a 5°C warming. The ^{13}C shift required the addition to the ocean-atmosphere reservoir of several thousand gigatons of ^{13}C-depleted carbon. Early thinking attributed these isotope shifts to CO_2 produced by the oxidation of methane-stored continental margin clathrate deposits. But this left open the question as to the nature of the precursor responsible for the sudden release of such a large quantity of methane (Kennett and Stott, 1991).

blip corresponded to a warming of about 5°C. Depending on the isotopic composition of its source, the three per mil carbon isotope decrease required the addition of at least one billion tons of carbon. If the CO_2 was produced by the oxidation of thermogenic methane, with a $\delta^{13}C$ of about -35‰, and if the Paleocene Ocean contained the same amount of inorganic carbon as today's (i.e., 36,000 billion tons), then a $\delta^{13}C$ drop of three per mil in ocean ΣCO_2 would have required the addition of on the order of 3000 billion tons of carbon. Were it volcanic CO_2, with a $\delta^{13}C$ of -5 per mil, the amount needed to drop the δ13C of marine carbon by three per mil would be huge - on the order of 20,000 billion tons of carbon. On the other hand, if it were swamp methane ($\delta^{13}C$ -60‰), the required amount of carbon would be only about 1500 billion tons of carbon.

In a paper published in 2002, Deborah Thomas made what I consider to be a spectacular discovery by analyzing individual foraminifer shells from ODP 690. She focused on three species of foraminifera: one surface-dwelling, one intermediate-depth dwelling, and one bottom-dwelling. In each case, she found that none of the shells formed during the interval of ^{13}C decline (Fig. 7-3). Rather they had either pre-PETM $\delta^{13}C$ values or PETM $\delta^{13}C$ values. This suggests that the transition period was short in duration.

An extremely puzzling result of her study is that the transition for the intermediate depth foraminifera is shifted up core by 10 cm. In that depth interval, intermediate-depth-dwelling foraminifer shells with pre-PETM $\delta^{13}C$ values coexist with surface-dwelling foraminifer shells with PETM $\delta^{13}C$ values. Based on the sedimentation rate, this interval of coexistence lasted about 10 thousand years. A similar situation was found for benthics. Those with pre-PETM $\delta^{13}C$ values coexisted with surface dwellers with PETM $\delta^{13}C$ values for 40 cm (i.e., ~40 thousand years). In both cases, the transition was abrupt. No shells with intermediate ^{13}C values were found. How could this be?

The most obvious explanation for this sequence is that it took about 10 thousand years for the water containing ^{13}C-depleted CO_2 to penetrate to intermediate depths and about 40 thousand years for it to penetrate the bottom. But, this is highly unlikely! Today, mixing to intermediate

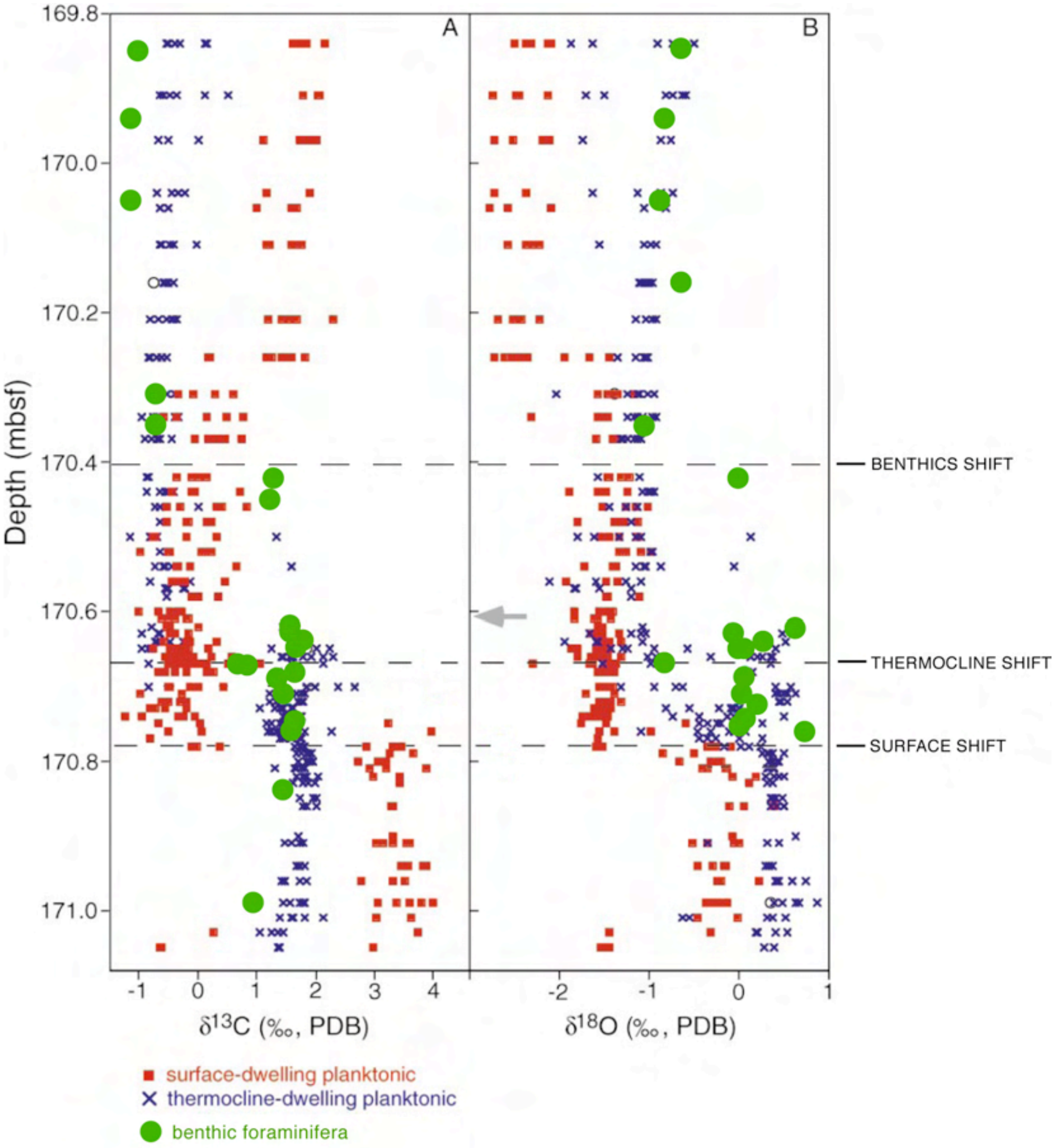


Figure 7-3. In an attempt to better constrain time required to accomplish the isotope jumps recorded in ODP690, Thomas and her coworkers made measurements on individual foraminifera shells. This eliminated the possibility that intermediate isotopic compositions were the result of mixing pre-PETM shells with PETM shells. To their surprise, they found no surface-dwelling foraminifera with intermediate carbon isotope compositions. Further, the same was the case for foraminifera living in the thermocline and also those living on the sea floor. But to their puzzlement, these latter transitions were respectively 10 and 40 cm up core from that for the surface dwellers. Based on the estimated rate of sediment accumulation, these offsets correspond to about 10 thousand and 40 thousand years. The obvious explanation is that it took this long for the carbon to get to the ocean's interior. But, as there are a number of reasons to reject this scenario, the offsets remain an enigma (Thomas et al., 2008).

depth is accomplished in less than one hundred years and to the bottom in less than one thousand years. Even though the 5°C warmer surface ocean temperatures must have temporarily strengthened the density stratification, it is highly unlikely that it would take 40 thousand years to break down this enhanced stratification. Further, in the same core, enhanced dissolution of $CaCO_3$ in deep sea sediments was underway in less than 40 thousand years after the PETM onset. If the CO_2 required to dissolve $CaCO_3$ got down there in less than 40 thousand years, then the ^{13}C-depleted CO_2 must have as well. Despite much thought, I have come up dry in my attempts to explain these offsets. In order to resolve this seeming dilemma, the 690 site should be revisited. Instead of hundreds of isotope measurements on single shells, thousands should be performed. Also, the abundances of each species should be determined.

The picture is not so clear for the oxygen isotope results for the same set of ODP 690 shells. For both those formed at the surface and those formed at intermediate depth, some shells do have $\delta^{18}O$ values lying in between the two extremes.

In 2003, Dennis Kent of Rutgers University published a paper suggesting that it was a comet that delivered the CO_2. His case was based on the sudden appearance of single domain magnetic nanoparticles. Unlike the chains of magnetic particles made by bacteria, single domain particles characterize extra-terrestrial material. The comet hypothesis has the advantage that it avoids the problem that a precursor was required to heat the ocean enough to break down the clathrates in continental margin sediments. Kent's comet hypothesis does not require such a precursor. Although an alluring idea, this hypothesis has fallen largely on deaf ears. Critics point out that there were no extinctions of note. Yet, a comet large enough to deliver the required amount of carbon should have devastated life.

The next important step in understanding the PETM came when Jim Zachos of the University of California, Santa Cruz obtained a set of five sediment cores ranging in depth from 2.7 to 4.8 km on the Walvis Ridge in the South Atlantic (Fig. 7-4). Each showed the same abrupt negative shift in carbon isotope ratios seen in ODP 690. In addition, for four of the cores the

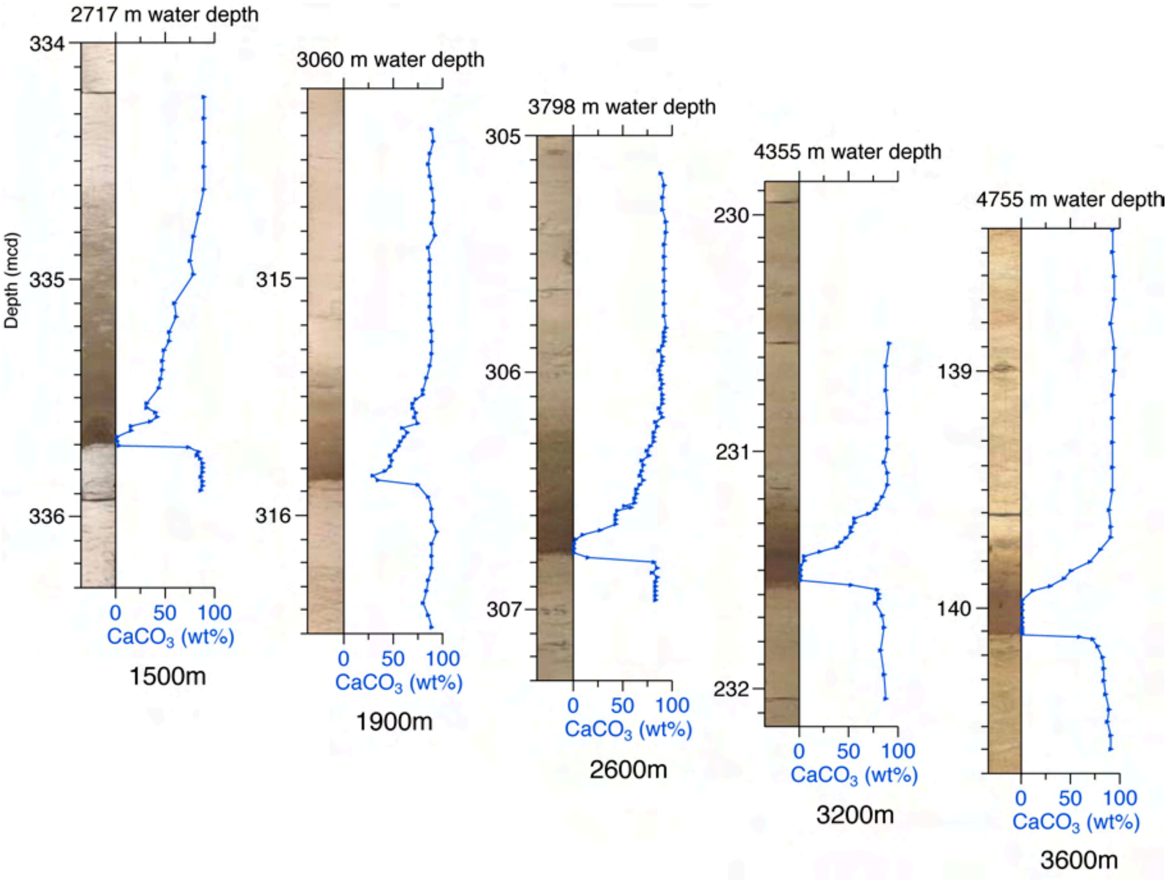


Figure 7-4. Records of $CaCO_3$ content versus depth in a series of five cores taken on the slope of the Walvis Ridge (ODP Site 208). In each an abrupt drop marks the onset of the PETM event. In four of the cores, there is an interval during which all the $CaCO_3$ reaching the sea floor was dissolved. It is estimated that this site has sunk by about 1200 meters in the last 55 million years. The original water depths are shown beneath each column. The color bars show the transition from $CaCO_3$-rich sediment (light) to $CaCO_3$-poor sediment (dark) (Zachos et al., 2005).

$CaCO_3$ content of the sediment just above the carbon isotope shift goes to zero. As the sediments deposited below and above the PETM are rich in $CaCO_3$, the absence of $CaCO_3$ suggests that when the CO_2-laden water reached the deep sea it reduced the carbonate ion concentration pushing the calcite saturation horizon up the water column. This shift exposed the sediments to water undersaturated with calcite. In each core, there was a time interval when little calcium carbonate accumulated. This upward shift in the depth of the calcium carbonate saturation horizon created an imbalance between production of calcite by planktonic organisms and its burial on the sea floor. Too much was being dissolved. As a result, the ocean's carbonate ion inventory grew. This buildup caused the saturation horizon to move back down the water column. The shallowest of the sediments were the first to experience a return to supersaturation. It took progressively longer for cores at greater depths (see Fig. 7-5).

The duration of the low ^{13}C interval was considerably longer than that for the dissolution interval (Fig. 7-6). In today's ocean, the turnover time for carbon is on the order of 100 thousand years. If it were the same at the time of the PETM, then the demise of the ^{13}C anomaly should have had an exponential folding time of about 70 thousand years. As can be seen, it was on the order of 25 thousand years. But inconsistent with expectation, the decline did not begin until about 45 thousand years after the onset of the PETM. In an attempt to model the shape of the $\delta^{13}C$ records, Richard Zeebe, of the University of Hawaii, found it necessary to introduce a second injection of about 1500 billion tons of carbon stretched over a period of about 40 thousand years. One way to explain this lag in the onset of the ^{13}C decline would be to call on the heating by cometary CO_2 to drive the release of clathrate-bound methane. In this case, the CH_4 cart would be behind the CO_2 horse instead of in front of it.

This is how things stood until Schaller and Wright published stable isotope records for a series of cores from across the state of New Jersey. Each penetrated the PETM. Their interest arose when Jim Wright offered to split one of the Jersey margin cores previously obtained by his colleague Ken Miller. He was surprised to note that just above the Paleocene–Eocene boundary,

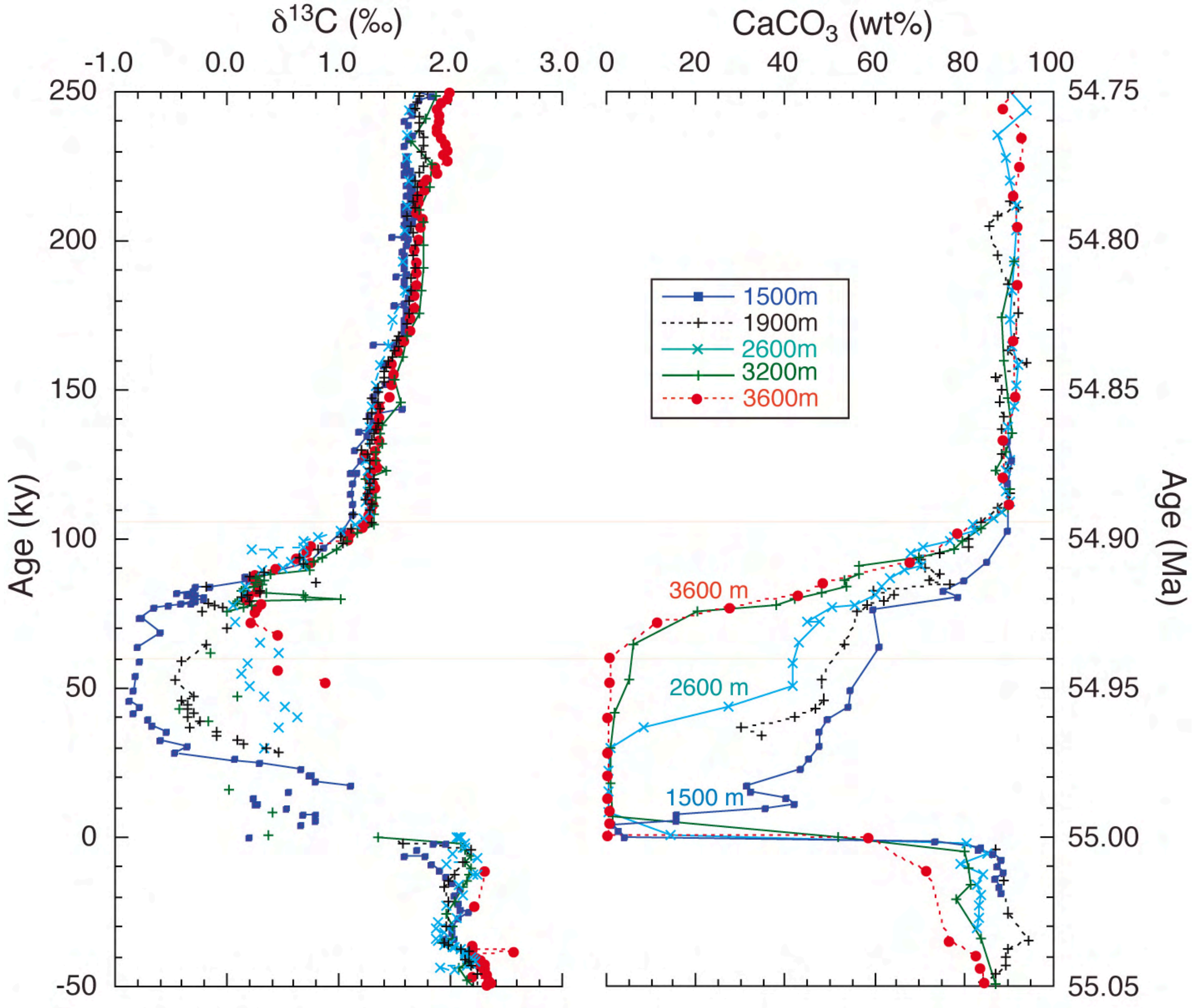


Figure 7-5. Composite of δ^{13}C and CaCO$_3$ records for the Walvis Ridge cores plotted against time rather than depth in the sediment column. The duration of the ^{13}C anomaly in all five cores is estimated to be just under 100 kyrs. However, the duration of the CaCO$_3$ event varies with water depth. The reason is that, as the excess CO$_2$ was neutralized, the compensation horizon migrated down the water column. The water depths are those reconstructed for the time of the PETM (Zachos et al., 2005).

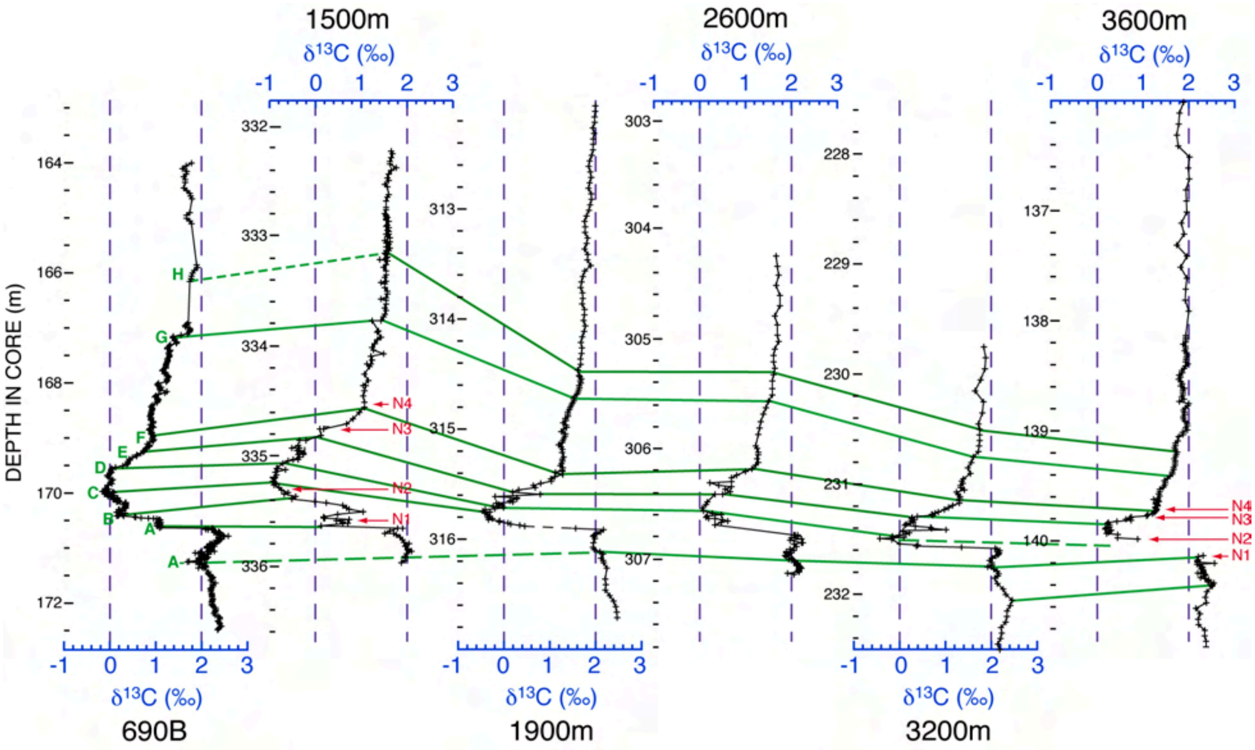


Figure 7-6. Carbon isotope records for ODP 690 and for the five cores from ODP site 208 on the Walvis Ridge. In each, the ^{13}C drop is about 2 per mil. The tie lines are based on a coccolith stratigraphy. The water depths for the Walvis cores are those reconstructed for the time of the PETM (Zachos et al., 2005).

the sediment was layered. There were about 700 such layers with a thickness averaging two centimeters. Although they initially regarded the layering as primary, they have subsequently been forced to admit that they are instead artifacts of drilling (i.e, in drilling parlance, “biscuits”). However, Schaller and Wright remain convinced that each biscuit is an annual layer (i.e., that the shearing during drilling follows seasonally weak sedimentary intervals). They are currently analyzing samples from PETM outcrops as a test of this idea.

In order to see whether they recorded the drop in ^{13}C seen in deep sea cores, Schaller and Wright performed a detailed isotope analyses on one of the cores. As foraminifera shells are exceedingly rare and very small, Schaller and Wright were forced instead to make their ^{13}C and ^{18}O measurements on bulk carbonate. To their amazement, they found that a ^{13}C drop of 3.5 per mil occurred in over an interval of just 13 layers (Fig. 7-7). A corresponding ^{18}O drop of a little over one per mil was also documented.

The question then arose as to what time interval these layers represented. They proposed that they were annual. To test this, Schaller and Wright produced a highly detailed ^{18}O record for the thirteen layers documenting ^{18}O cycles consistent with seasonal changes in temperature.

The next step was to do carbon and oxygen isotope analyses on bulk $CaCO_3$ for 6 other of the New Jersey cores (Fig. 7-8). In each they found a ^{13}C decline of similar duration. But the magnitude ranged from 8.1 per mil to 3.5 per mil decreasing to the east (i.e., with distance from the then coast line and hence with water depth) (Fig. 7-9). In each core, the ^{13}C drop occurred in thirteen layers. In addition they arranged to make isotope measurements on cores obtained from Maryland and Virginia by the U.S. Geological Survey. They are also layered and record the carbon isotope dip. In one of these cores the ^{13}C decline was a whopping 12 per mil. Based on the trend of the magnitude of the ^{13}C decline with distance from the coast line (i.e., with water depth), they estimate that at the onset of the decline the atmosphere’s δ^{13}C was a whopping 20 per mil.

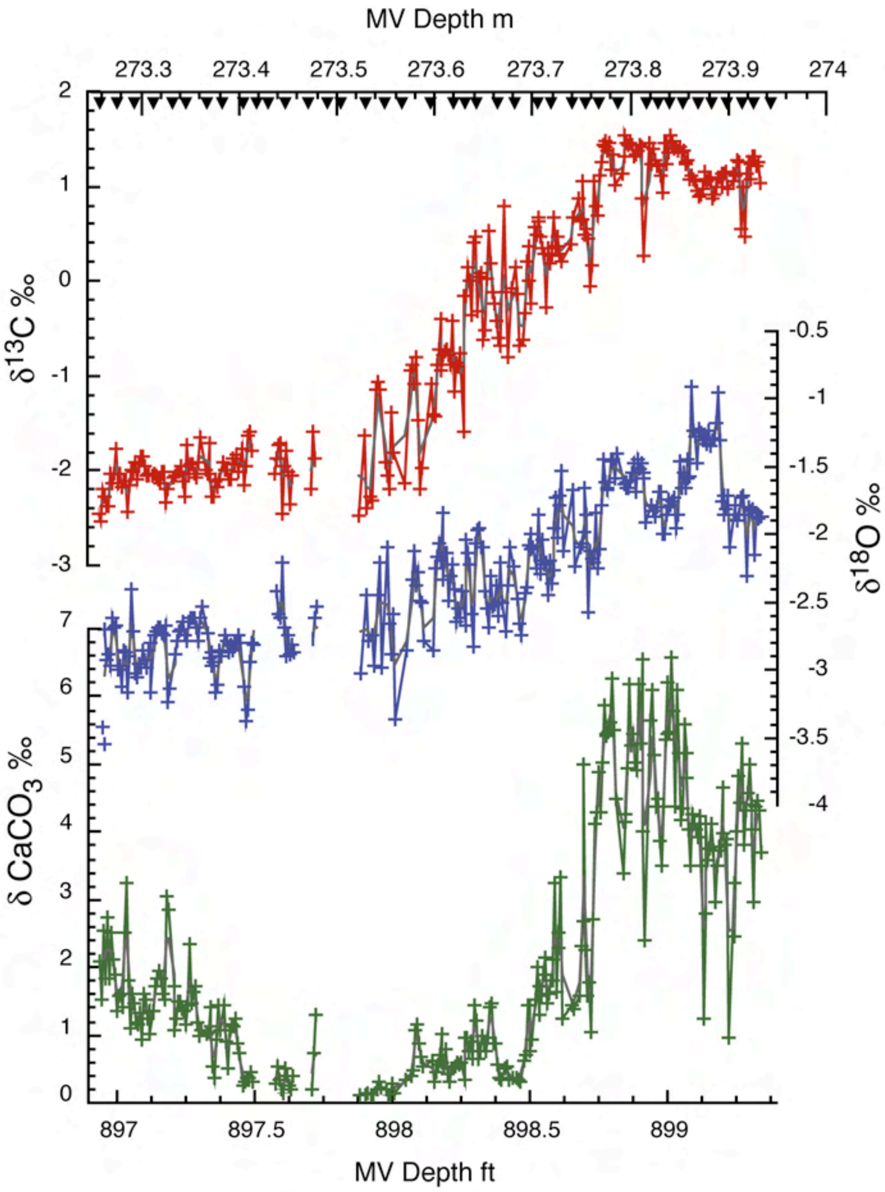


Figure 7-7. Stable isotope (on bulk CaCO$_3$) and CaCO$_3$ content records across the PETM onset as recorded in a core from Millville, New Jersey. Assuming that each layer represents one year, the ^{13}C decline occurred in just 13 years. The magnitude of the decline is about 4 per mil. The ^{18}O decline during this same interval corresponds to a cooling of roughly 4°C. By contrast, the drop in CaCO$_3$ content occurred an order of magnitude faster (i.e., in about 2 years). Were an abrupt addition of isotopically-light CO$_2$ to take place over today's ocean, the CO$_3^{=}$ ion response would be ten times faster than the isotopic composition response (Wright and Schaller, 2013).

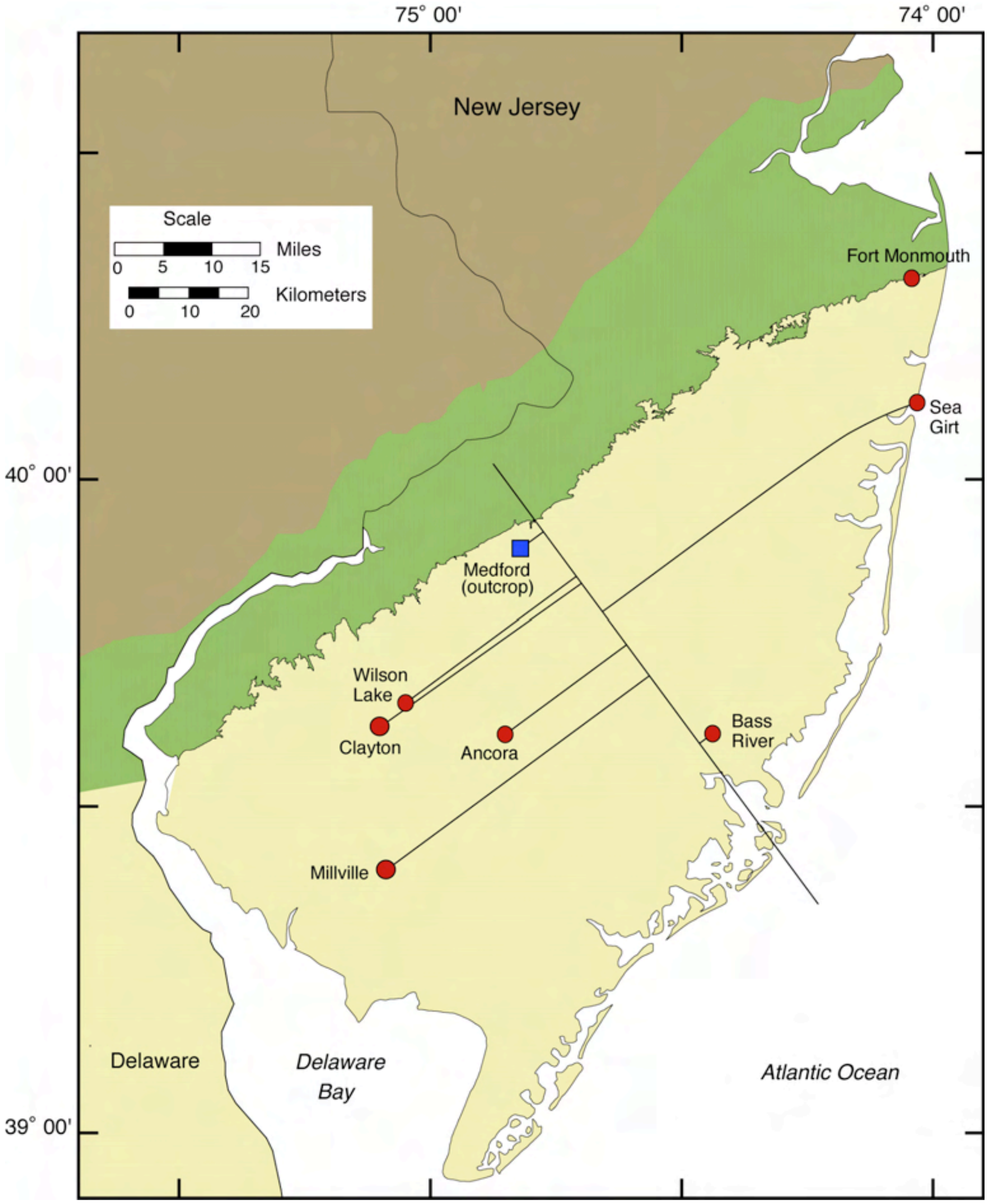


Figure 7-8. Map showing the locations of the cores (circles) in which the onset of the PETM is preserved. The green to yellow boundary marks the transition from Cretaceous to Cenozoic sediment. The square is for an outcrop of the Marlboro clay which contains layers similar to those seen in the cores.

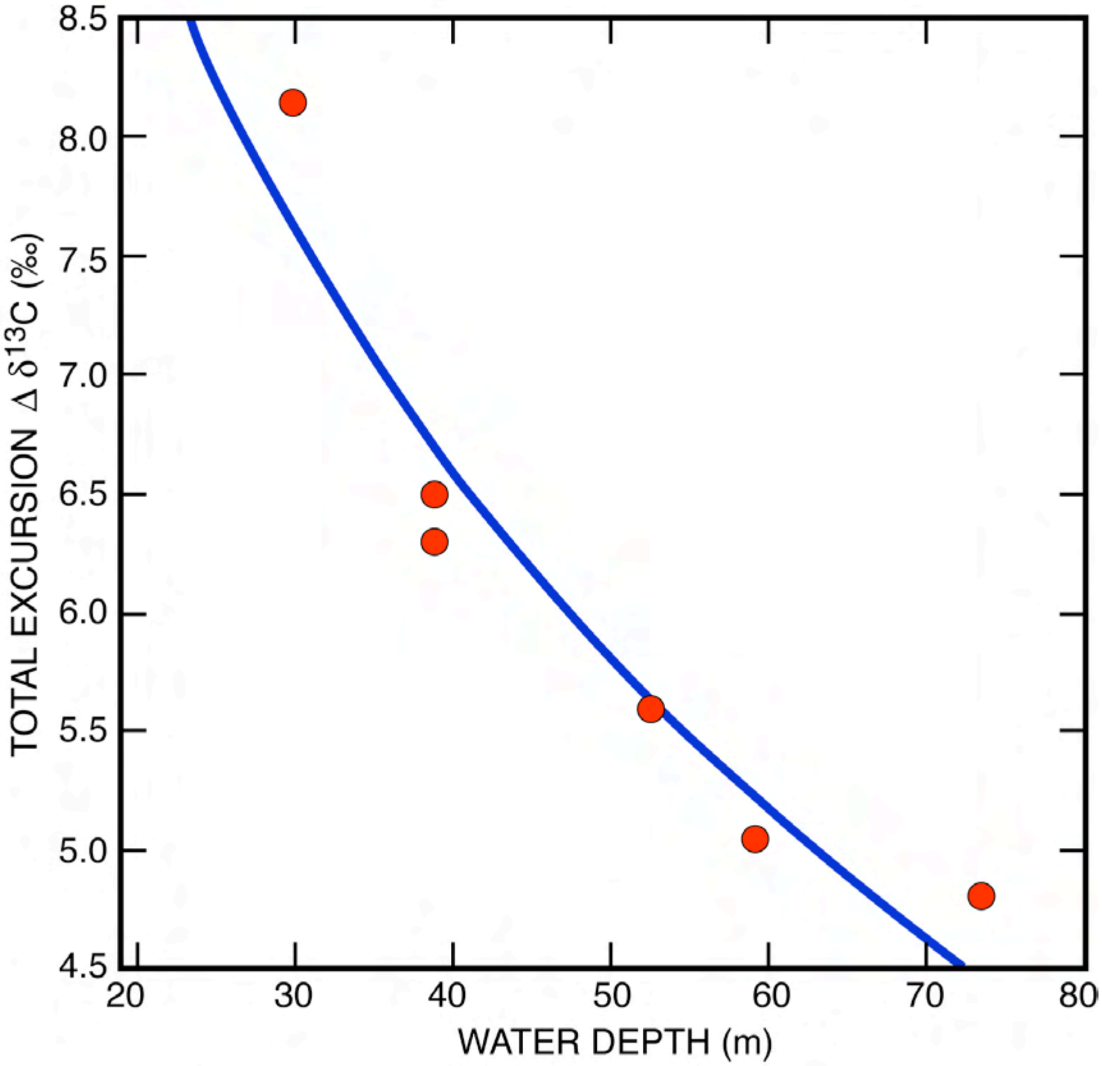


Figure 7-9. Magnitude of the ^{13}C decline as a function of distance from the PETM coastline. Based on present-day shelf morphology, the distances have been converted to water depths (Wright and Schaller, 2013).

If, as Wright and Schaller propose, each biscuit represents one year, then the only way to explain their results is to call on an extraterrestrial source. As asteroids contain only traces of carbon, this source must be a comet. Comets are thought to contain about 10 percent carbon as CO and CO_2 ice. Much of the rest is water ice. Spectral analyses from ground-based telescopes reveal a range of carbon isotope compositions extending from $\delta^{13}C = 0$ to $\delta^{13}C = -50$ per mil, assuming that the amount of carbon delivered by this object was 1000 gigatons. Then its radius would have to have been about 15 km.

It is interesting that Zachos published results from the Jersey margin Bass River site which is further off shore than the others, and consequently has a much lower accumulation rate and hence a much larger abundance of foraminifera shells. He obtained $\delta^{13}C$ records for three different planktic species and also for bulk $CaCO_3$. He found the same sharp 3 per mil drop in $\delta^{13}C$ for bulk $CaCO_3$ as he did for the planktic species. This strengthens Schaller and Wright's claim that bulk $CaCO_3$ is a reliable stand-in for foraminifera shells (more on this below).

In addition to the isotope measurements, Wright and Schaller did $CaCO_3$ analysis on the core from Melville, N. J. Prior to the PETM ^{13}C decline, the $CaCO_3$ content of the sediment averaged 4 to 5 percent by weight. Within two years after onset of the ^{13}C decline, the content dropped to a few tenths of a percent. If, as Wright and Schaller propose, the input of the ^{13}C deficient CO_2 to the atmosphere was instantaneous, then the tenfold more rapid response of the calcium carbonate content compared to that of the carbon isotope ratio is to be expected. Changing the carbon isotope composition involves all the dissolved inorganic carbon (i.e., CO_2+HCO_3-+$CO_3^=$). Changing the saturation state for calcite involves only the $CO_3^=$ ion. As in today's surface ocean there is ten times more dissolved inorganic carbon than $CO_3^=$ ion, it takes about ten times longer to adjust the isotope composition than to adjust the acidity.

The shape of the carbon isotope response declines in the first decade of the PETM are consistent with those following the input of ^{14}C to the atmosphere as a result of H-bomb tests conducted by Russia, Great Britain and the United States in 1962. They were carried out in anticipation of the nuclear test ban which went into effect on January 1, 1963. The CO_2 labeled with this nuclear test ^{14}C was rapidly taken up by the ocean. The time trend of the rise in the ^{14}C to ^{12}C ratio in the surface ocean mixed-layer was similar to the time trend of the uptake of PETM CO_2 (labeled with a ^{13}C deficiency) by the coastal waters off North America (see Fig. 7-10).

Taken together, the results of the ^{13}C analyses present a picture which resembles that generated by the 1962 H-bomb tests which produced a large amount of radiocarbon. It drove the ^{14}C to C ratio in the atmospheric CO_2 up to 1.7 times the pre-test level. This radiocarbon was then transferred into the surface ocean and terrestrial biosphere. By measuring the ^{14}C to C ratio in coral growth rings, the time history of ocean uptake has been reconstructed. As can be seen in Figure 7-10, the time required for the surface ocean to achieve its maximum was about 15 years. After that, it began a slow decline.

Based on the Schaller and Wright time scale (i.e., one year per biscuit), the time history of ^{13}C to ^{12}C ratios in bulk $CaCO_3$ from the New Jersey PETM sediment cores bears an amazing resemblance to that for H-bomb ^{14}C to C.

Those who don't accept the Schaller-Wright time scale point out that as the origin of the small amount of fine-grained carbonate is not known, it just as well could be terrestrial in origin. If so, its deficiency could be diagenetic. One argument against this is based on the relationship between $\delta^{18}O$ and $\delta^{13}C$ for all these samples (including those from Virginia and Maryland). As can be seen in Figure 7-11, $\delta^{13}C$ values range over 15 per mil (42.4 to -13 per mil). The $\delta^{18}O$ values range over only about 5 per mil. There is no clear correlation between $\delta^{18}O$ and $\delta^{13}C$. This being the case, diagenesis can perhaps be ruled out.

I suppose that one might call on some combination of marine and soil carbonates with similar $\delta^{18}O$ values but a large difference in $\delta^{13}C$ (the soil carbonate deficient in the heavy isotope). But, if so, one would have to finesse an explanation as to why on a millennial time scale, one could reproduce the pattern shown in Figure 7-10 including the dependence on water depth.

A fierce debate focused on the record in Marlboro clays currently rages. The question is: are they annual? One aspect of this debate is whether they are real or whether they are a product

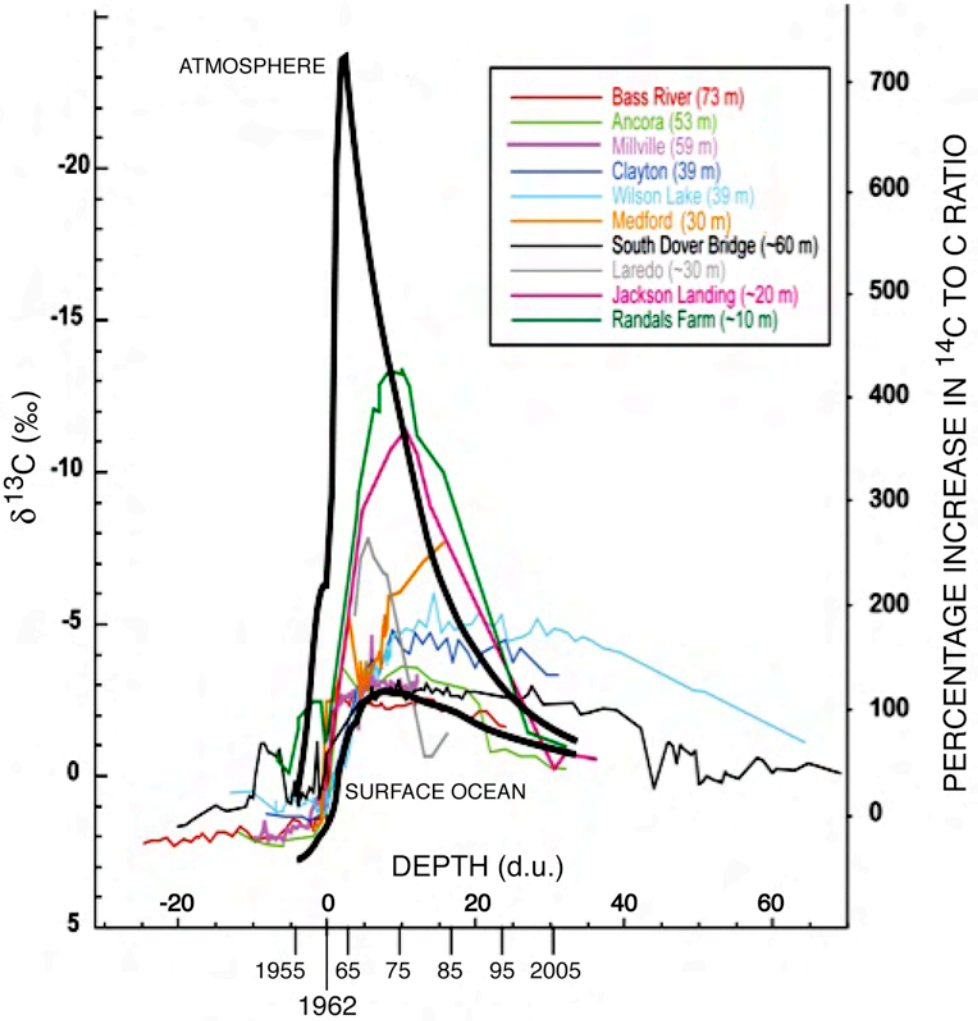


Figure 7-10. Comparison between the ^{14}C spike created by hydrogen bomb test carried out late in 1962 (just before the treaty banning atmospheric atomic bomb tests went into effect) and the ^{13}C-deficient CO_2 added to the atmosphere at the onset of the PETM. The heavy black curves show the time history of the ^{14}C excess in the atmosphere and ocean. The other curves show the time histories of ^{13}C deficiency in coastal PETM-age sediments. The depth scale for the latter has been set to emphasize the similarity between the two. The water depths for the coastal cores are listed. For comparison, the depth of the mixed layer at the sites of the annually banded corals used for the surface ocean ^{14}C reconstruction is about 45 meters. Based on the Schaller and Wright's biscuit counting, the peaks in ^{13}C curves occur at about 13 layers after the onset. If, as they assume, the biscuits are annually spaced, then the 13 years from onset to peak compares well with the ten years required to achieve the ^{13}C peak. On the other hand, if the ^{13}C time scale is a millennium or so, rather than a decade, it is difficult to create a scenario to explain these records.

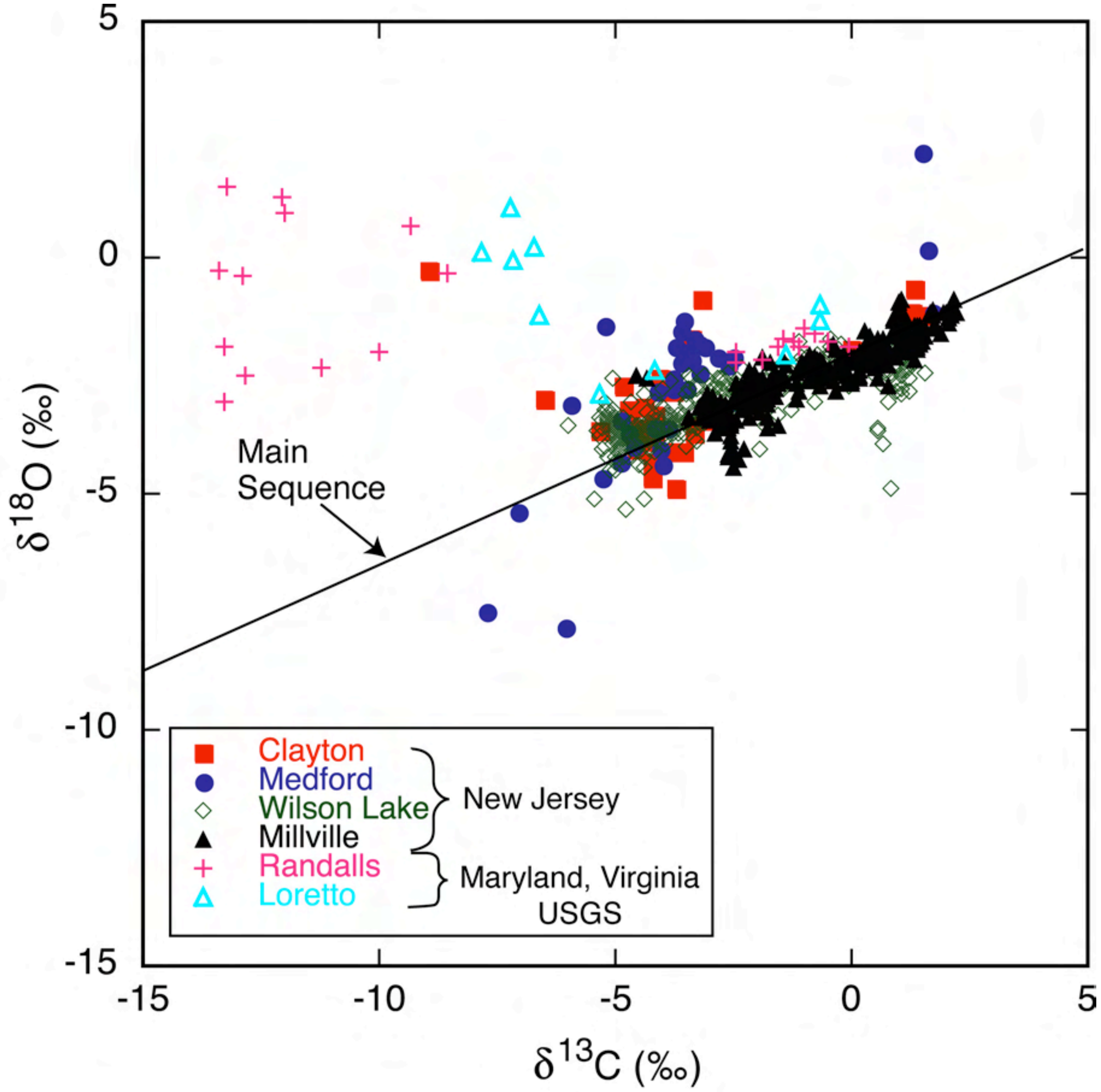


Figure 7-11. Plot of $\delta^{18}O$ versus $\delta^{13}C$ on bulk $CaCO_3$ for four sediment cores from New Jersey and two USGS cores from New Jersey and Virginia. As can be seen, the two which show the greatest range in $\delta^{13}C$ (15 per mil) have a smaller range for $\delta^{18}O$ (5 per mil). Only the core from the Millville site has the sense of correlation expected for diagenetic alteration (i.e., the greater the extent of alteration the more negative the values for both isotopes). The most negative $\delta^{18}O$ values (i.e., those less than -5 per mil) are for samples with very low $CaCO_3$ content (i.e., less than one-half percent).

of drilling. It is well known that rotary drilling creates ‘biscuits’ separated by injections of the clay laden drilling fluid. Faced with this, Schaller and Wright are forced to admit that this is also the case for their cores. But they would like to think that the injections occurred along weak layers formed to a single season. They point to the cycles in ^{18}O seen in each layer. The key to this question lies in the Marlboro sediments exposed in the Medford stream cut. Wright is currently studying a block of sediment obtained during the summer of 2014.

A second issue of contention is the origin of the ^{13}C and ^{18}O changes seen in these cores. The detractors call on diagenetically altered $CaCO_3$ eroded from the coastal shore lands. One argument against this is the agreement between the isotope records in bulk $CaCO_3$ and foraminifera in the Bass River core. But the detractors would say it has a much higher ratio of marine calcite to terrestrial calcite so the diagenetic signal is overwhelmed. The supporters would challenge the detractors to explain why in each of the cores the $\delta^{13}C$ drop starts abruptly and is complete in just 13 ‘biscuits’.

If the isotopic composition of the bulk carbonate were recording diagenesis or production ion soils one might expect that the ^{18}O might be more strongly impacted than the ^{13}C. As can be seen in Figure 7-11, this is not the case. The range of $\delta^{13}C$ values is twice that for ^{18}O. Also, most of the results for the New Jersey cores fall along a single trend where a change of 3 per mil in $\delta^{13}C$ corresponds to a 1.2 per mil in $\delta^{18}O$.

If the magnitude of the atmospheric CO_2 rise associated with the PETM could be reliably estimated, then this event could be used as a means to constrain the sensitivity of the Earth’s temperature to the atmosphere’s CO_2 content. Simulations carried out in ocean-atmosphere models suggest that in the climate system’s present configuration a doubling of CO_2 would warm the planet by 3.5 ± 1.0°C. The models also suggest that the dependence is logarithmic rather than linear. So, if an increase in CO_2 content from its preindustrial content of 280 parts per million to 560 ppm drives a warming of 3.5°C, in order to get a 7.0°C warming, would require a second doubling (i.e., from 560 to 1120 ppm).

Lamont-Doherty's Bärbel Hönisch employed the boron isotope pH proxy to estimate the change in CO_2. She analyzed planktonic foraminifera from a core from the North Pacific and found that the $\delta^{11}B$ dropped from 15.7 ± 0.2‰ before the PETM to 15.0 ± 0.2‰ during the PETM, a drop of 0.7 ± 0.3‰ (Fig. 7-12). During the post PETM recovery interval, it rose back to about 15.6‰. If the isotope ratio in bulk boron in the ocean at the time of the PETM were known, it would be possible to say by what factor the CO_2 content of the atmosphere rose. I say 'factor' because like pH, the warming by CO_2 is also logarithmic. So, for example, if the PETM pH change were 0.6 units, the CO_2 content of the PETM surface waters would have risen by a factor of four. Such a rise would have warmed the planet by about 7°C.

Summarizing. If the Marlboro clay is annually layered, then the only way to explain the large and extremely rapid decline in the ^{13}C to ^{12}C ratio of its $CaCO_3$ is to call on an instantaneous injection of several thousand billion tons of CO_2. Only a comet with a diameter of ten kilometers or so could deliver such a large dose. Were it a comet, there would be no need for a precursory warming. Further, it is possible that the impact could explain the very unusual character of the Marlboro clay. It would also provide an explanation for the absence of planktic foraminifer shells with intermediate $\delta^{13}C$ values in sediment core ODP 690.

Another lingering question has to do with the location of the crater created by the impact of this huge object? In this regard it must be kept in mind that it took a couple of decades to locate the crater associated with the K-T boundary asteroid. Further, if the comet hit somewhere on the 40 percent of the ocean floor that has been subducted during the last 55 million years, it will never be found. Of the remaining 60 percent of the Earth's surface, about half is land and half sea floor. Hence, if it exists, there is a 50 percent chance that it lies beneath the sea surface. One clue as to where to search involves the Iceland hot spot plume. It reached the surface about 55 million years ago. Were it a consequence of the comet impact, one place to look would be on the opposite side of the globe (i.e., in the vicinity of New Zealand's South Island).

Yet another point of contention as to why only benthic foraminifera became extinct at the time of the PETM. As the K-T asteroid caused the extinction of half the species then extant, how

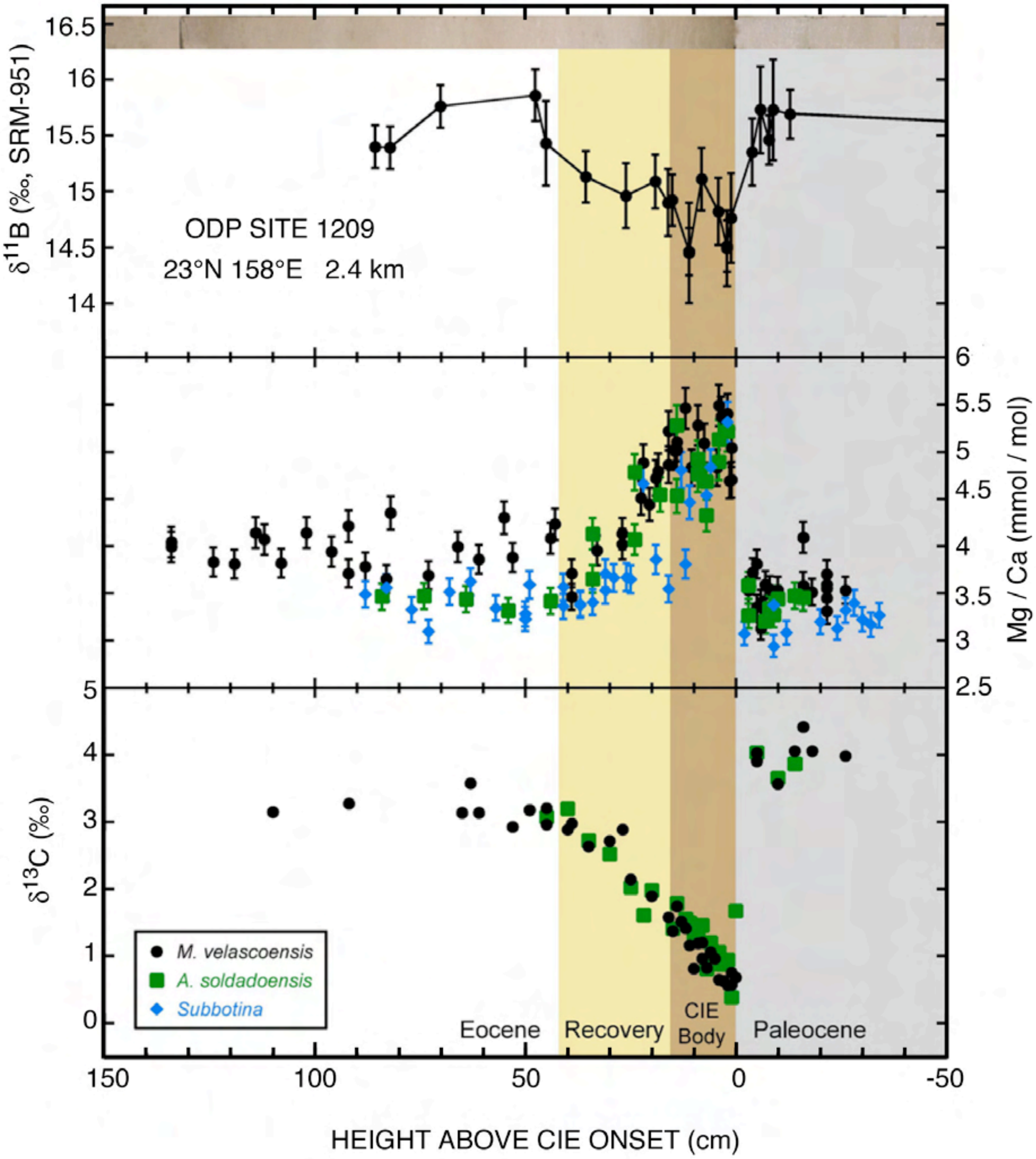


Figure 7-12. Boron isotope (pH), magnesium/calcium (ΔT) and carbon isotope measurements ($\Delta\Sigma CO_2$) on three species of planktic foraminifera from a core located on the North Pacific's Shatsky Rise (Penman et al., 2014). The warming indicated by the Mg to Ca ratio and the ^{13}C decline are consistent with those obtained for cores from the Atlantic Ocean. The 0.8 per mil drop in $\delta^{11}B$ is interpreted by the authors to be the consequence of a 0.3 unit drop in pH (and hence a doubling of the atmosphere's CO_2 content).

could it be that a comet of similar size didn't do even more damage? Comets travel faster than do asteroids. It must however be kept in mind that there is no agreement regarding the link between the massive K-T extinctions and the asteroid impact. Even so, it is very difficult to believe that a cometary impact of this magnitude would do so little damage to Earth life. Hence, the absence of widespread extinctions is clearly the weakest link in the comet scenario.

All this is worth sorting out. The reason is that the PETM constitutes the closest geologic analogue to the on-going build-up of fossil-fuel CO_2 in our atmosphere and ocean. The amount of CO_2 added by the comet is similar in magnitude to that which would be produced if we were to burn a major fraction of our fossil-fuel reserves. It already tells us a few important things. First, the injection of CO_2 warmed the Earth by about 5°C. The very long duration of the PETM suggests that the initial warming triggered the release of clathrate-bound greenhouse gases. As more records are obtained and more thought is given, the PETM analogue will become an ever more valuable guide to what lies before us.

References for Chapter 7

Kent, D. V., B. S. Cramer, L. Lanci, D. Wang., J. D. Wright, and R. Van der Voo (2003), A case for a comet impact trigger for the Paleocene/Eocene thermal maximum and carbon isotope excursion, *Earth Planet. Sci. Lett. , 211*, 13-26.

Penman, D. E., B. Hönisch, R. E. Zeebe, E. Thomas, and J. C. Zachos (2014), Rapid and sustained surface ocean acidification during the Paleocene-Eocene Thermal Maximum, *Paleoceanography*, doi: 10.1002/2014PA002621, in press.

Storey, M,.R. A. Duncan, and C. C. Swisher III (2007), Paleocene-Eocene Thermal Maximum and the opening of the Northeast Atlantic, *Science*, *316*, 587-589.

Thomas, D. J., J. C. Zachos, T. J. Bralower, E. Thomas, and S. Bohaty (2002), Warming the fuel for the fire: Evidence for the thermal dissociation of methane hydrate during the Paleocene-Eocene thermal maximum, *Geology*, *30*(12), 1067-1070.

Wang, H., D. V. Kent, and M. J. Jackson (2013), Evidence for abundant isolated magnetic nanoparticles at the Paleocene-Eocene boundary, *PNAS*, *110*(2), 425-430.

Wright, J. D., and M. F. Schaller (2013), Evidence for a rapid release of carbon at the Paleocene-Eocene thermal maximum, *PNAS, 110*(40)*,* 15908-15913.

Zachos, J. C., *et al.* (2005), Rapid acidification of the ocean during the Paleocene-Eocene Thermal Maximum, *Science*, *308*, 1611-1615.

Zachos, J. C., S. Schouten, S. Bohaty, T. Quattlebaum, A. Sluijs, H. Brinkhuis, S. J. Gibbs, and T. J. Bralower (2006), Extreme warming of mid-latitude coastal ocean during the Paleocene-Eocene Thermal Maximum: Inferences from TEX86 and isotope data, *Geology*, *34*(9), 737-740, doi: 10.1130/G22522.1.

Zachos, J. C., S. M. Bohaty, C. M. John, H. McCarren, D. C. Kelly, and T. Nielsen (2007), The Palaeocene-Eocene carbon isotope excursion: constraints from individual shell planktonic foraminifer records, *Phil. Trans. R. Soc. A*, *365*, 1829-1842, doi: 10.1098/rsta.2007.2045.

Zeebe, R. E., J. C. Zachos, and G. R. Dickens (2009), Carbon dioxide forcing alone insufficient to explain Palaeocene-Eocene thermal Maximum warming, *Nature Geoscience*, *2*, 576- 580, doi: 10.1038/NGEO578.

Addendum

As I was in the late stages of this revision, I learned that the $\delta^{13}C$ analysis of foraminifera shells associated with the New Jersey and also the Delaware PETM cores showed that, instead of the 8 to 15‰ negative excursions given by bulk $CaCO_3$, the foram excursion was more like 3‰ (i.e., about the same as that for open ocean cores). In my estimation, this puts the comet scenario in doubt. Hence, the change in the title of this chapter.

Chapter 8

Continents Collide

Something happened 51 million years ago that set the Earth on a cooling course which continues today. I make a case here that this change in course was a consequence of the collision between the northward-drifting Indian subcontinent and Asia (Bouilhol et al., 2013). Not only did this collision create the Himalayan Mountains and Tibetan Plateau, but it forced a reconfiguration of the movement of the Earth's crustal plates. I suspect that, as a result, the continents have become ever more mountainous and the ocean ever 'deeper'.

As shown in Figure 8-1, four marine isotope records undergo important trend changes at this time. These changes occur at the same time as India made contact with the island arc bounding the southern margin of Asia (see Fig. 8-2). At this same time, as recorded in the Emperor seamount chain, the Pacific plate changed directions. It took a sharp left turn changing from its northern course to one to the northwest. Sharp and Claque (2006) showed that this shift occurred 50 million years ago (Fig. 8-3). Further, at this time, the Pacific plate began to subduct along arcs stretching from southern Japan (35°N) to the Island of Palau (7°N). Based on precise argon and uranium-lead ages, Reagan et al. (2013) place this onset at 51.1 ± 1.5 million years ago. This onset matches the time when the Pacific plate deviated to a more westerly track.

That polar cooling commenced at this time is well documented by the ^{18}O isotope record kept in benthic foraminifera (see Fig. 8-1). About 15 percent of this change is the result of the growth Antarctic ice cap (i.e., storage of ^{18}O deficient water in ice). The remaining 85 percent is the result of cooling of deep sea (about 10°C). It is not necessary to separate these two contributions because they both are the result of a planet-wide cooling.

The most reasonable scenario explaining this cooling is that the CO_2 content of the atmosphere was drawn down. One way this might have happened is that, as a result of the plate reorganization, the rate of CO_2 release from the planet has undergone a continuing decline. The other is that in order to counter a steady increase in the tendency toward an oversupply of

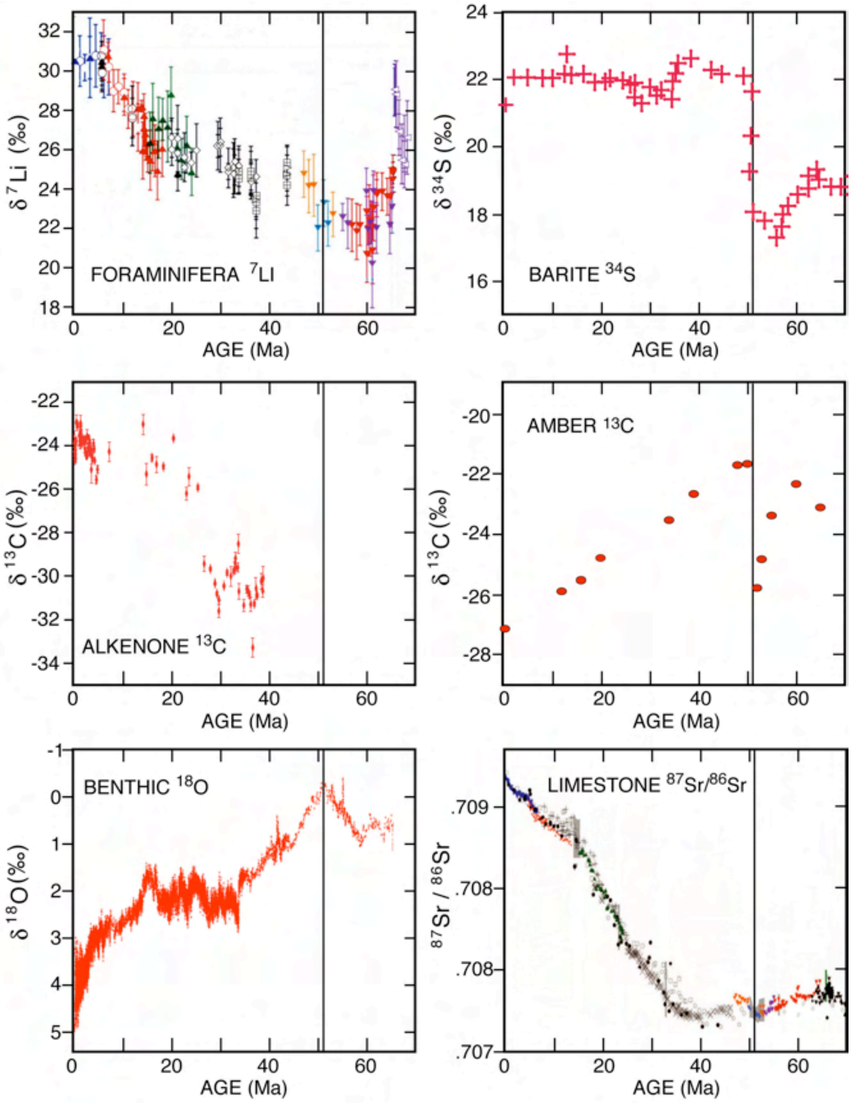


Figure 8-1. Summary of the records for 6 proxies extending back into the Cenozoic. For four of them, something important happened 51 million years ago. For the ^{34}S record kept in marine barite, it was an abrupt upward shift from one steady state value to another. For the ^{13}C record kept in amber, it was an abrupt upward shift followed by a decline which continues right up to the present. For the ^{7}Li record kept in marine foraminifera shells, a steady increase commenced at this time. The same is the case for the ^{18}O record kept in benthic foraminifera shells. The ^{13}C record for alkenones contained in coccoliths covers only the last 38 million years. Unlike that for amber which decreases toward the present, that for alkenones increases. Finally, while the ^{87}Sr record kept in foraminifera shells also shows steady increase, for reasons discussed in the text, its onset is delayed by 10 to 15 million years. The less complete Mg to Ca record also begins a climb roughly 50 million years ago (see Fig. 8-2). It seems clear that these changes were initiated by the collision of India with Asia. But, as many potential linkages exist, a number of different scenarios could be put forward.

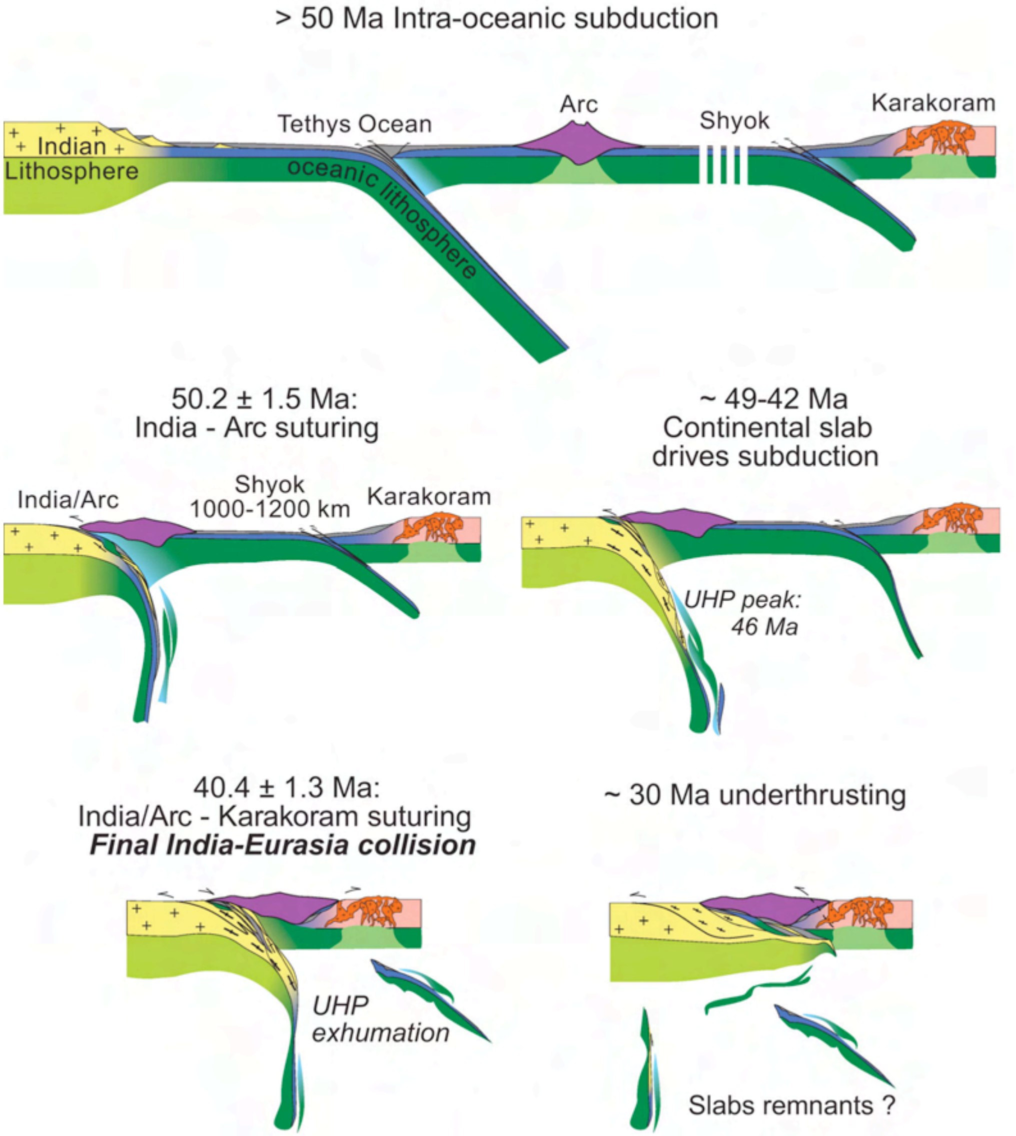


Figure 8-2. Geodynamic sketch of the collision sequence of India with Asia (Bouilhol, et al., 2013). Note that the age assigned to the onset of the collision is 50.2 ± 1.5 million years.

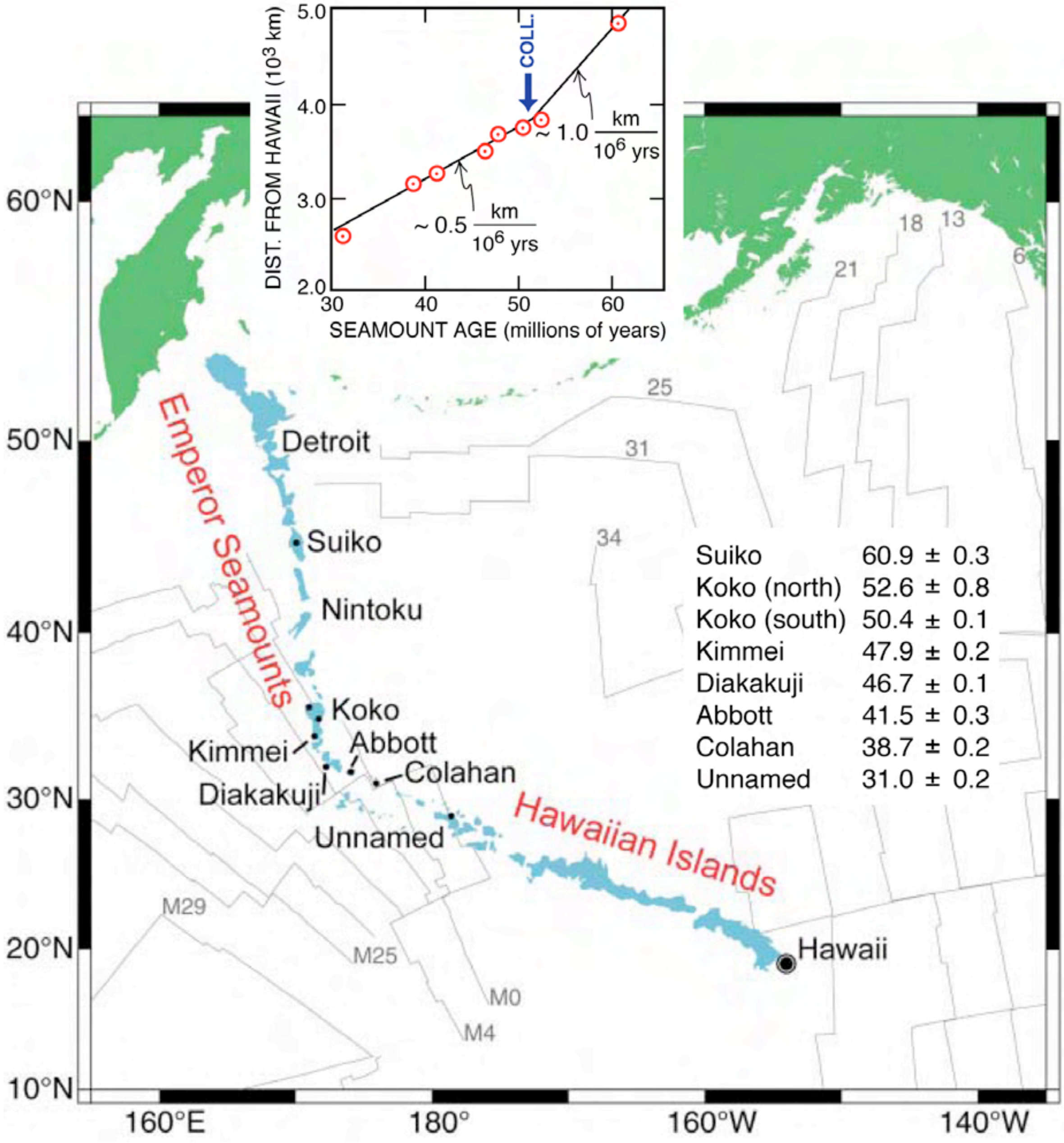


Figure 8-3. Map of the Emperor Seamount – Hawaiian Island trace. Sharp and Clague (2006) obtained argon ages on 7 of the sea mounts demonstrating that the bend in the trace occurred close to the time that India collided with Asia (see arrow). As shown in the inset, not only did the direction of the Pacific Plate's movement change, but also its rate of drift slowed by a factor of two.

calcium derived from the chemical weathering of silicate rocks, the CO_2 content of the atmosphere has been forced to steadily decline (see Chapter 2). But, before discussing this further, we should consider the attempts to reconstruct the atmosphere's CO_2 content.

The most widely discussed proxy for past atmosphere CO_2 content is that based on the ^{13}C to ^{12}C ratio for the alkenones produced by *Emiliania huxleyi*. This choice is favored because coccolithophorids live in the surface-ocean mixed layer. Therefore there is no concern with regard to the presence of respiration CO_2. By focusing on a single chemical compound, issues with regard to compound to compound $\delta^{13}C$ difference is eliminated. However, this choice does not eliminate the dependence of the fractionation factor on PO_4 content of the water in which the coccoliths grew (see Chapter 3). There is also a question regarding use of HCO_3^- at low CO_2 concentrations. Finally, *Emiliania huxleyi* has been in existence for only the last 38 million years.

The alkenone ^{13}C record suggests that there was a drop in the atmosphere's CO_2 content during the last 38 million years. But there is a major difference between the shape of the carbon dioxide decline determined in this way and that for the polar temperature record (Fig. 8-1). While most of the CO_2 decline appears to have taken place before 20 million years ago, roughly half of the cooling occurred after this time. Further, the stepwise drop in CO_2 content occurred right in the middle of a 20 million-year time interval during which the $\delta^{18}O$ for benthic forams remained nearly constant.

It is interesting to note in this connection that a quite different trend is found for the $\delta^{13}C$ record for bulk organic matter contained in deep sea sediment. Falkowski et al. (2004) provide summaries of the carbon isotope records for both deep sea bulk $CaCO_3$ and bulk organics (Fig. 8-4). If one takes the difference between these records as a measure of the trend of pCO_2 atmospheric CO_2 content, then a different picture emerges. Most of the increase occurs during the last 20 million years.

Franks et al. (2014) outline a more quantitative way to employ leaf stomata as a paleo CO_2 proxy. They calculate the stomatal resistance from a combination of stomatal number

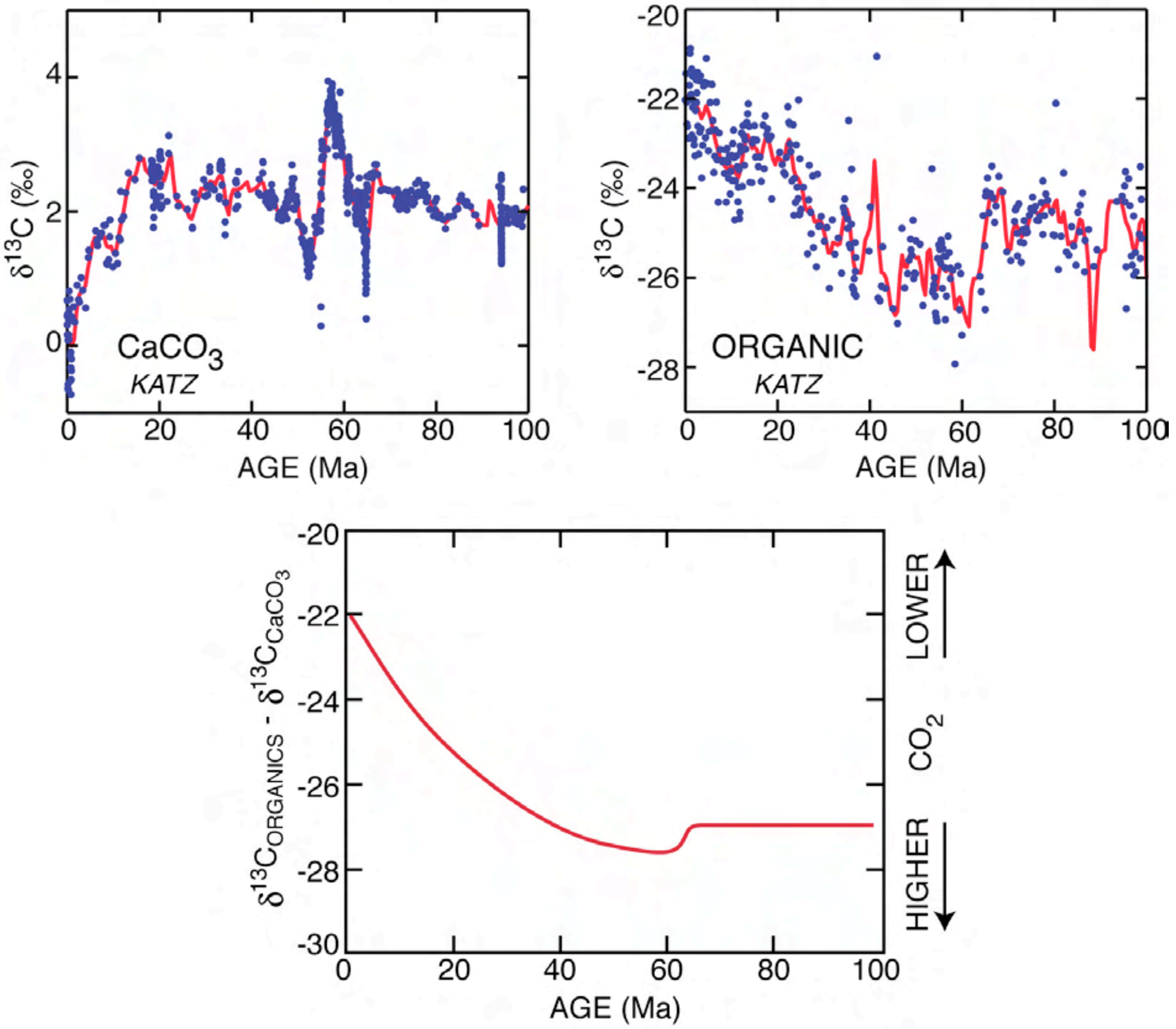


Figure 8-4. Records covering the last 100 million years of the ^{13}C to ^{12}C ratio in marine $CaCO_3$ and marine organic matter (Falkowski et al., 2004). Of particular interest is the drop in δ^{13}C of $CaCO_3$ which has taken place over the last 10 or so million years. Rather than indicating a reduction in the fraction of carbon buried as organic matter, it more likely reflects a replacement for C-3 by C-4 grasses. Also of interest is the 6 per mil drop in the δ^{13}C of marine organic material. The simplest explanation for this drop would be that it is the result of a decrease in the atmospheric CO_2. However, unlike the record for alkenones which shows little change over the last 20 million years, most of the change in the δ^{13}C difference between marine organic material occurs during this time interval.

and aperture size and the δ^{13}C between the leaf carbon and atmosphere CO_2. Instead of being restricted to a single species, this approach allows any C-3 plant to be employed. Although this new approach has yet to be extensively exploited, Franks et al. do present a record covering the time interval from 10 million to 2 million years. As is the case for alkenones, they find that no significant change occurred during this time interval.

Two of the proxy records (Fig. 8-1) show pronounced jumps at the time of the collision (i.e., 51 million years ago). One is Paytan's ^{34}S record for marine barite. At this time, the δ^{34}S undergoes a four per mil upward jump. If both the isotopic composition of the sulfur added to the ocean and the isotope fractionation factor during sulfur reduction are assumed to have remained the same, then in order to explain this jump, it is necessary to call on an increase in the fraction of the sulfur deposited as pyrite. This could have been triggered by a drop in the atmosphere's O_2 content. Such a drop would require that the collision exposed a large amount of reduced carbon and/or of reduced iron. The other is an abrupt 4 per mil drop in the δ^{13}C ratio in amber. Tappert et al. attribute this to a drop in atmospheric O_2. If so, it would be consistent with the shift toward pyrite deposition suggested by the sulfur isotope record.

However, before getting carried away with explaining the δ^{13}C drop record by an O_2 drop in amber, we must face up to an apparent contradiction between the δ^{13}C record for amber and that for marine alkenones during the last 38 million years. The alkenone δ^{13}C becomes 4 per mil more negative and the amber δ^{13}C becomes 4 per mil less negative. If, as most believe, the changes in δ^{13}C are driven primarily by the availability of CO_2, then there is no way to reconcile these opposing trends. One thought is that as O_2 reacts with rubisco releasing CO_2 depleted in ^{13}C, if this CO_2 is recycled, an increase in O_2 could explain the decline in ^{13}C. Perhaps land plants are more sensitive to O_2 changes and marine plants more sensitive to CO_2 changes. Were this the explanation, then the ^{13}C record for amber is telling us that over the past 35 million years O_2 increased and the alkenone record tells us that CO_2 decreased. However, the 8 per mil differential shift between alkenones and amber over the last 40 million years stretches credibility. First, as today's photosynthetic fractionation is about 20 per mil, then in order to explain the 8 per mil differential shift between marine organics and terrestrial amber, about 40 percent of the CO_2 utilized by today's plants would have to be recycled in the leaf. Finally, the few available growth experiments involving changes in the O_2 to CO_2 ratio suggest that recycling can account for only one, or at most two per mil, rather than 8. In any case, it is critical to conduct experiments aimed at quantifying the impact of O_2 on the $\delta^{13}C$ of terrestrial plants. As we have no oxygen proxy, it would be exciting if the $\delta^{13}C$ in land plants were more sensitive to O_2 than to CO_2.

After remaining quite low for 100 million years, the Mg to Ca ratio in sea salt began to rise. This increase occurred during the last 50 million years (Fig. 8-5). The leading explanation for this change is that it was a consequence of a drop in sea level associated with the plate reorganization caused by the collision. To understand why requires a look at the sources and sinks of the element Mg. Today it is gained mainly from the weathering of the continent and lost mainly to hydrothermal circulation through the hot ridge crests. The sink is documented by the observation that the 300°C water exiting ridge-crest hydrothermal vents contains no magnesium. Its absence demonstrates that the magnesium contained in the seawater drawn into the ridge flanks is removed by reaction with hot basalt.

There is one other potentially important pathway for Mg removal. Much of the limestone deposited in shallow inland seas has been converted to dolomite. This requires the replacement of half the calcium atoms with magnesium atoms. As sea level was drawn down, the vast inland seas in which dolomite formed were gradually eliminated. As a result, $CaCO_3$ deposition shifted ever more to the deep sea. The analysis of deep-sea cores penetrating the entire deep sea sediment column reveals that no conversion to dolomite occurs in this environment.

As the inventory of Mg in the ocean depends on its rate of removal, if 50 million years ago half of the Mg was removed at ridge crests and half as dolomite, then other

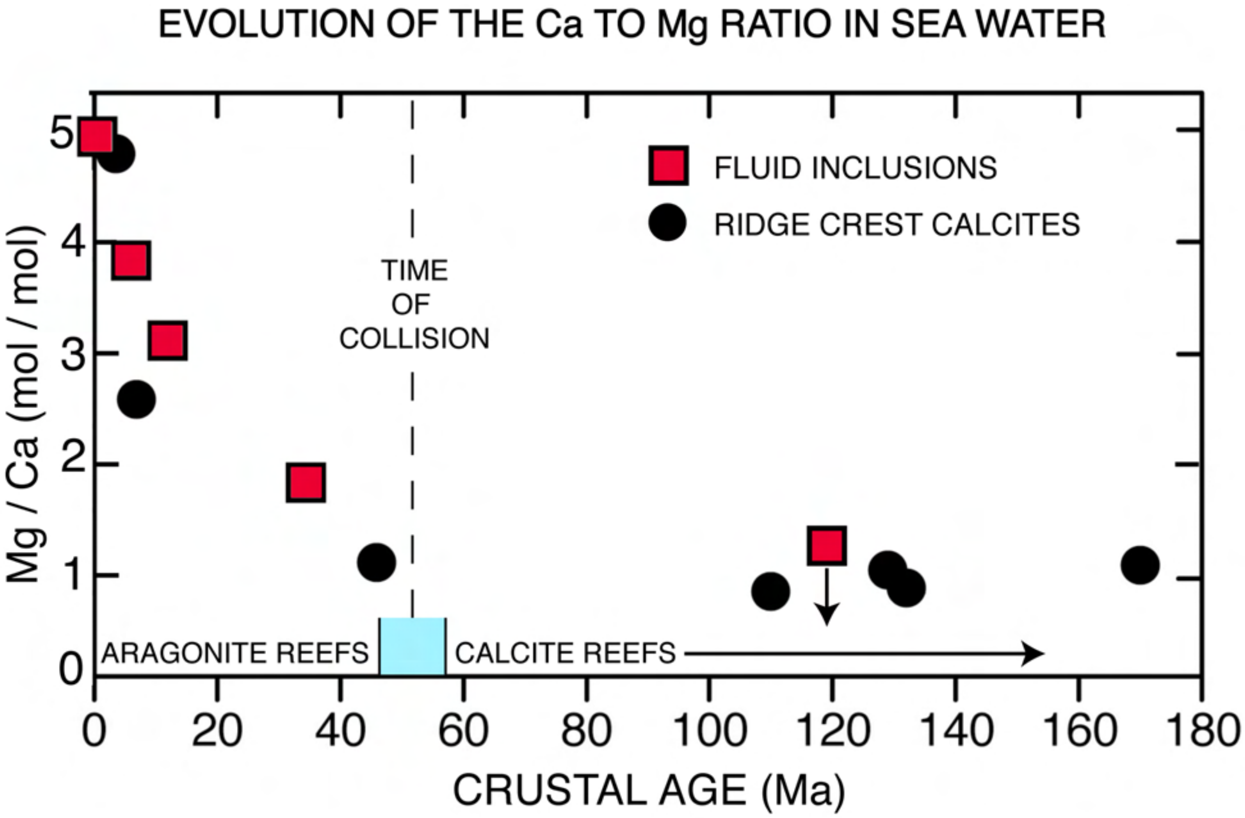


Figure 8-5. Time trend of Mg to Ca ratios in seawater as reconstructed from measurements on halite-hosted fluid inclusions (Brennan et al., 2013) and from those on ridge crest calcites (Coggon et al., 2010). Although both proxies have serious shortcomings, they tell consistent stories. The Mg to Ca ratio in seawater has risen by about a factor of five over the last 180 million years. Most of this rise has occurred during the last 50 million years. Consistent with this trend is the observation by Hardie (1996) that prior to about 50 million years ago, reefs were formed mainly by calcite producing organism. Since this time, aragonite producers have come to the fore. Lab experiments show that calcite precipitation is favored at low Mg to Ca ratios and aragonite at high Mg to Ca ratios.

things being equal, a shutdown of dolomite formation would have halved its removal rate and thereby doubled its concentration in seawater. Further, the release of Ca as the result of dolomite formation would have been cut off. The result would be a drop in its concentration in seawater. As it is not possible to quantify the magnitude of these changes, the explanation remains unverified. Further, other things may not have been equal. But if a reduction in dolomite formation is the major cause, then the rise in the Mg to Ca ratio in seawater is likely a consequence of the collision of India with Asia.

It is unclear, to me at least, why the δ^7Li in seawater has been getting larger for the last 50 million years. I would like to believe that whatever it is that it reflects the tendency toward an increase in the supply of silicate weathering-derived calcium to the sea. But, the situation is complicated. We know that rivers are enriched in ^{7}Li relative to igneous rocks and suspect that this enrichment is the result of preferential uptake of ^{6}Li during clay mineral formation both on land and on the sea floor. Hence, one way to explain the trend in δ^7Li in seawater would be to call on an increase in isotope fractionation as the land and sea cooled. If so, δ^7Li becomes a proxy for temperature though it tells us nothing about the supply of Ca. Another possibility is that the proportion of lithium removed from seawater at a high temperature and a low temperature has been decreasing with time. A third would be to propose that the amount of lithium undergoing multiple cycles of chemical erosion followed by uptake into clay minerals has been increasing. Clearly, more field studies, such as that carried out by Pogge von Strandmann and Henderson, will have to be conducted before this situation clarifies.

It is also interesting to note that the onset of the rise in the ^{87}Sr to ^{86}Sr ratio did not occur 50 million years ago. Rather, it was delayed by more than 10 million years. Such a delay is broadly consistent with John Edmond's leucogranite scenario. It involves deep burial and metamorphism of granites. The metamorphism leads to a redistribution of the radiogenic ^{87}Sr between high Rb to Sr ratio minerals (micas and pyroxenes) to low Rb to Sr minerals (plagioclase and calcite). As the latter minerals are far more susceptible to chemical weathering than the former, when millions of years later the leucogranites are exhumed to the surface, a greater portion of the ^{87}Sr is released in solution rather than remaining trapped in insoluble minerals. Hence, if Edmond's scenario is the correct one, then a delay of ten million years is not unreasonable.

Another thing to be explained is why, except for that for the isotopic composition of marine sulfur, all the records shown here are characterized by changes that continue right up to the present. Initiated by the collision 50 million years later, they continue. Several things likely contributed. One is mountain building. Another is the progressive lowering of sea level. Yet another is the progressive increase in the sculpting of mountains by glaciers. Why there was no change in δ^{34}S during this time interval remains unexplained.

As this book is about Earth carbon, of particular interest to us are proxies which tell us something about the ocean's cycling of this element. As we have seen, we can say something about four ocean constituents important to this cycle. They are: the CO_2 content of surface water and the Ca^{++}, $CO_3^{=}$, PO_4, and O_2 contents of deep water. Let's begin with dissolved oxygen. As already discussed, the oxygen isotope record kept in benthic foraminifera shells provides a means to reconstruct deep ocean temperature. As the density of seawater increases with decreasing temperature, deep waters are supplied from the polar regions. Hence, the 10°C cooling of the deep ocean over the last 50 million years tells us that the polar regions have cooled. As they cooled, the solubility of O_2 increased. At 10°C, seawater takes up about 275 μmol O_2 per liter. At its freezing point (-1.8°C), this amount rises to about 360 μmol O_2 per liter. Further, if Tappert et al. are correct that the O_2 content of the atmosphere has increased during the last 50 million years, 50 million years ago the O_2 content of newly formed deep water would have been even lower. Yet, the presence of benthic foraminifera everywhere in the deep sea at that time tells us that the O_2 content did not dip to zero anywhere in the open deep sea. This is curious, as in today's deep North Pacific, O_2 drops to a scant 7 percent of its saturation content (i.e., to 25 μmol per liter).Yet during the Eocene, when initial O_2 contents were much lower as indicated by the presence of benthic foraminifera shells, the deep ocean never went anoxic.

One way to explain why there was no anoxia is to call on a lower amount of utilized PO_4 (i.e., some combination of a lower total PO_4 and a lower efficiency of PO_4 utilization). But, we have seen that the $\delta^{13}C$ difference between planktic foraminifera shells formed in oligotrophic surface waters and those formed on the sea floor was not significantly different 50 million years ago than it is now. (Fig. 8-6). Hence it appears that the ΣCO_2 to P ratio was close to the same difference. So, both the ΣCO_2 and PO_4 concentrations must have been lower than now 50 million years ago.

In thinking about this, it must be kept in mind that if part of the deep sea were to become anoxic, a greater fraction of the organic matter produced in the surface ocean would go uneaten. As a consequence, more PO_4 would be buried and its matching O_2 would accumulate in the atmosphere. In this way, the anoxia would be eliminated. As both the inventories of O_2 in the atmosphere and PO_4 in the sea can be changed on the time scale of 20 or so thousand years, it is possible that the feedback involves the inventories of both of these constituents.

As we have seen, the water depth of the transition from $CaCO_3$-rich to $CaCO_3$-poor sediment serves as a proxy for the product of the concentrations of Ca^{++} and $CO_3^{=}$ in the deep sea. A recent study, centered on the equatorial Pacific Ocean, provides a more detailed and accurate reconstruction than any of the earlier summaries (Pälike et al. 2012). Instead of focusing only on time when the core site subsided through the transition zone, the authors considered the entire record of $CaCO_3$ content. They found a number of cores where the $CaCO_3$ content underwent two $CaCO_3$-rich to $CaCO_3$-poor transitions. In other words, after subsiding below the value defining the compensation depth, the deep ocean CO_3 ion concentration went up. This record suggests that 35 million years ago compensation depth in the Pacific Ocean descended from about 3.8 km to 4.6 km and then about 18 million years ago when it rose half way back up again.

However, instead of telling us something about the change in the global deep ocean product of Ca and CO_3 ion concentrations, this finding could instead point to a change in

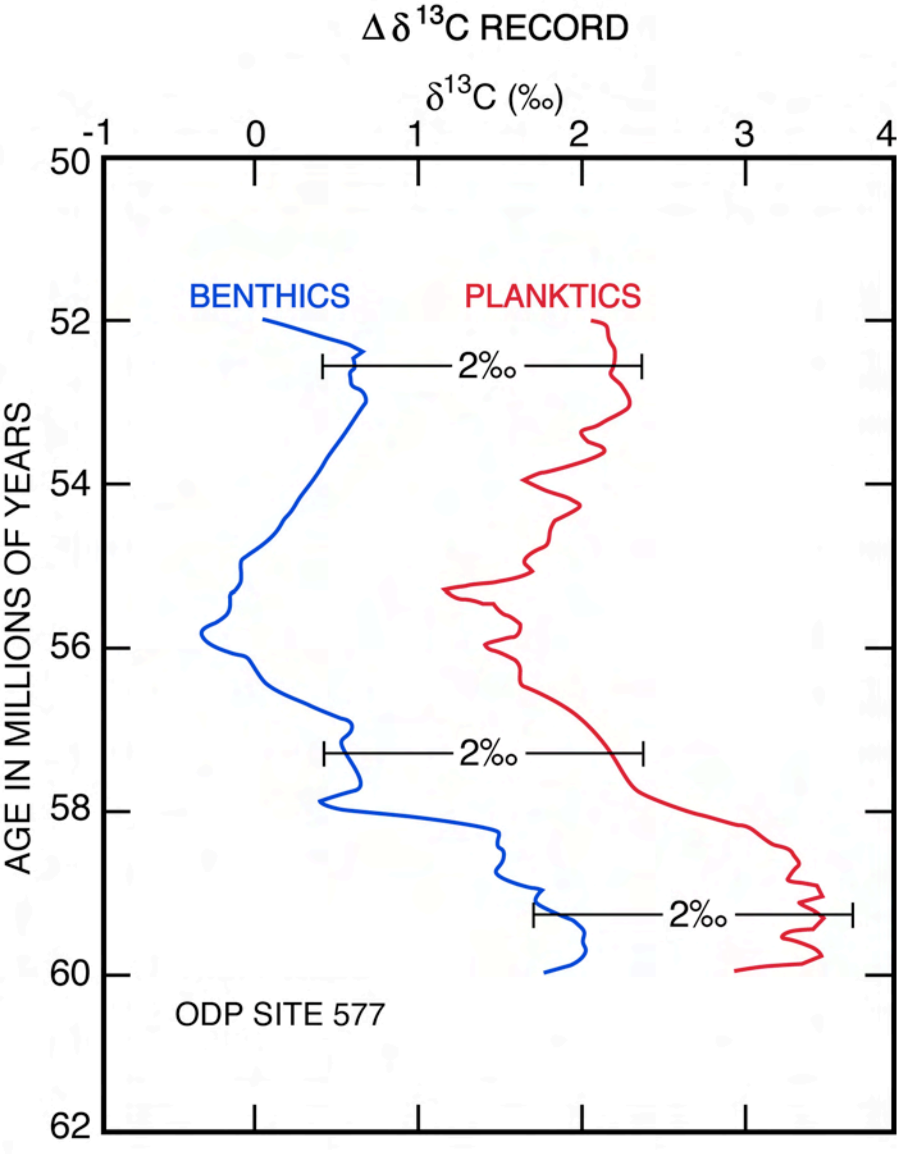


Figure 8-6. A record obtained by Rutgers University's Ken Miller of the $\Delta\delta^{13}C$ between coexisting planktic and benthic foraminifera shells. For a period of 9 million years, it remained close to -1.8‰. This suggests that 55 million years ago, the ratio of PO_4 to ΣCO_2 in the ocean was similar to today's.

where deep water formed. In today's ocean deep waters in the equatorial Atlantic have a CO_3 ion concentration averaging 105 μmol/kg. For the equatorial Pacific, the average is about 85 μmol/kg. As a result, the compensation depth in the Atlantic (~4.5 km) is deeper than that in the Pacific (~3.5 km). This difference is related to the fact that deep Atlantic waters contain only one half the amount of PO_4 and hence roughly half the amount of respiration CO_2 as those in the Pacific. This difference arises because deep water forms in the northern Atlantic but not in the northern Pacific. Hence the compensation depth changes could be related to some re-configuration of continents which altered the connectivity among the world's ocean basins. For example, several million years ago the gap between Central and South American closed off. Five million years ago, the Mediterranean Sea became isolated. Fifty-five million years ago, the passage between South America and the Antarctic Peninsula opened.

Equally important to where deep water forms is the transport of water vapor through the atmosphere. Today water vapor is transferred from the Atlantic to the Pacific. In so doing, it enriches salt in the surface Atlantic and depletes it in the surface Pacific. As a result, deep water forms in the northern Atlantic and not in the northern Pacific. These inter-ocean fluxes of water vapor would have been altered as the location of continents changed and as mountain chains came into being. For these and other reasons, the contrast between the compensation depths in the two oceans has likely changed with time. Because of this, it is important to obtain a record for the equatorial Atlantic of comparable quality to that which Pälike et al. (2012) obtained for the equatorial Pacific.

Further, it must be kept in mind that the global depth of $CaCO_3$ compensation is set by the need to dissolve the excess of $CaCO_3$ production over the delivery of ingredients. In other words, the global compensation depth serves as a proxy for the ratio of the rate of $CaCO_3$ production to the rate of ingredient supply. Were, for example, the ocean-wide compensation depth to drop from 3.6 km to 4.6 km, the increase in the product of $Ca^{++} x CO_3^{=}$ required to accomplish this would have been only about 15 percent. Hence, even when the fluctuations in compensation depth are taken into account, the $Ca^{++} x CO_3^{=}$ product has remained remarkably constant. This tells us that the amount of $CaCO_3$ produced by marine organisms has for the last 50 million years exceeded the supply of ingredients by several fold.

Curiously the global cooling which followed on the heels of the collision did not result in a significant change in the $\delta^{13}C$ trend for limestone. The $\delta^{13}C$ in marine $CaCO_3$ remained nearly the same from 50 million years to about 15 million years (Fig 8-4). During the last 15 million years, it underwent a 2 per mil drop. Part of this decrease is thought to be the result of the replacement of C-3 grasses with C-4 grasses. The reason is that the magnitude of carbon isotope fractionation is much smaller for the C-4 pathway than for the C-3 pathway.

In this connection an observation made by Utah's Thure Cerling is of interest. Based on carbon isotope measurements on the tooth enamel from fossil horses, he was able to show that during mid-Miocene (6 to 8 million years ago) horses went from eating C-3 to eating C-4 grass (Wang et al., 1994). As the horse teeth came from three continents hosting different species of grass, this shift must have been caused by some planet-wide environmental change. Today C-4 grasses thrive in the warm tropics and C-3 in cooler mid latitude. Hence, one explanation could be that the shift was the result of planetary warming. But all indications are that the planet was cooling rather than warming. The other possibility is that, as C-4 plants pump in CO_2, they have an advantage when the atmosphere's CO_2 content is low. This was Cerling's favored explanation. The problem is that neither the alkenone ^{13}C record nor that based on stomatal resistance suggests that CO_2 underwent a significant drop during that time interval. As horses eat grass and not tree leaves, this transition must have involved a conversion of C-3 grasslands to C-4 grasslands. So we are left with a dilemma. Clearly Cerling would favor the ^{13}C record for bulk marine organic matter (Fig. 8-5). It shows a steady increase during the last 20 million years. Are we being misled by the alkenone and stomatal records or is there some other environmental change which could account for this global transition? One possibility is that the places where these horses grazed became drier. Because they pump CO_2 into contact with the photosynthetic enzyme, C-4 grasses require less water than their C-3 brothers.

Rather than wave my arms and invent a clean-cut story to explain the proxy records covering the last 50 million years, I will restrict the discussion to what I consider to be the key observations. Something of lasting planet-wide importance was initiated 51 million years ago. It makes good sense that its trigger was the collision of India with Asia. This collision led to the closure of the Tethys Sea and the creation of the Himalaya Mountains and Tibetan Plateau. It also forced a reorganization of plate motion across the entire planet which I'd like to believe led to an elevation of the continents and a deepening of the ocean basins. We live with its consequences even today.

Clearly this collision had a major impact on the Earth's sulfur cycle. The isotope record in marine barite nails this down. It also appears that O_2 content of the atmosphere may have dropped. However, as the ^{13}C dependence on atmospheric O_2 remains poorly documented, we have no assurance that amber ^{13}C is a valid O_2 proxy. I doubt whether it is.

As recorded in the oxygen isotopes in benthic foraminifera, the polar regions began to cool close to 51 million years ago. One consequence was the growth of polar ice caps. This resulted in the further lowering of sea level and hence a further reduction of the area of inland seas. This cooling also led to the expansion of mountain glaciers. Both of these resulted in changes in weathering cycle on the Earth's surface. As a consequence, the concentrations of Ca and Mg (and likely SO_4 as well) in the ocean changed. Also, the δ^7Li in the ocean started its climb at this time.

There is no reason to believe that the ongoing drift toward an ever colder world will soon come to an end. Were it to continue for several tens of millions of years, it would lead to another snowball episode (Broecker, 2015). Although we humans are currently countering this trend by burning fossil carbon, as our supply of these fuels is limited, on the time scale of thousands of years, whatever we do in this regard will be erased. As this course toward cold was initiated by a catastrophe, perhaps yet another lies in the offing which will put the Earth's climate on yet another track.

References for Chapter 8

Bouilhol, P., O. Jagoutz, J. M. Hanchar, and F.O. Dudas (2013). Dating the India-Eurasia collision through arc magmatic records, *Earth Planet. Sci. Lett. 366*, 163-175.

Brennan, S. T., T. K. Lowenstein, and D. I. Cendon (2013), The major-ion composition of Cenozoic seawater: The past 26 million years from fluid inclusions in marine halite, *Am. J. Sci.*, *313*, 713-775, doi: 10.2475/08.2013-1.

Broecker, W. (2015), The collision that changed the world. *Elementa: Science of the Anthropocene*, in press.

Coggon, R. M., D. A. H. Teagle, C. E. Smith-Duque, J. C. Alt, and M. J. Cooper (2010), Reconstructing past seawater Mg/Ca and Sr/Ca from mid-ocean ridge flank calcium carbonate veins, *Science*, 1,114-1,117.

Edmond, J. M. (1992), Himalayan tectonics, weathering processes, and the strontium isotope record in marine limestones, *Science*, *258*, 1,594-1,597.

Falkowski, P. G., M. E. Katz, A. J. Milligan, K. Fennel, B. S. Cramer, M. P. Aubry, R. A. Berner, M. J. Novacek, and W. M. Zapol (2004), the rise of oxygen over the past 205 million years and the evolution of large placental mammals, *Science*, *309*, 2202-2204.

Franks, P. J., D. L. Royer, D. J. Beerling, P. K. Van de Water, D. J. Cantrill, M. M. Barbour, and J. A. Berry (2014), New constraints on atmospheric CO_2 concentration for the Phanerozoic, *Geophys. Res. Lett.*, *41,* doi: 10.1002/2014GL060457.

Froelich, F., and S. Misra (2014), Was the Late Paleocene-Early Eocene hot because Earth was flat? *Oceanography, 27*, 37-49.

Hardie, L. A. (1996), Secular variation in seawater chemistry: An explanation for the coupled secular variation in the mineralogies of marine limestones and potash evaporites over the past 600 m.y., *Geology*, *24*, 279-283.

Hayes, J. M., H. Strauss, and A. J. Kaufman (1999), the abundance of ^{13}C in marine organic matter and isotopic fractionation in the global biogeochemical cycle of carbon during the past 800 Ma, *Chemical Geology*, *161*, 103-125.

Holland, H. D. (1978), *The Chemistry of the Atmosphere and Ocean*, Wiley, New York, 369 pp.

Holser, W. T., and I. R. Kaplan (1966), Isotope geochemistry of sedimentary sulfates, *Chemical Geology*, *1*, 93-135.

Kent, D. V., and G. Muttoni (2013), Modulation of Late Cretaceous and Cenozoic climate by variable drawdown of atmospheric $p$$CO_2$ from weathering of basaltic provinces on continents drifting through the equatorial humid belt, *Clim. Past, 9,* 525-546.

Molnar, P. (2004), Late Cenozoic increase in accumulation rates of terrestrial sediment, *Annual Reviews of Earth and Planetary Sciences*, *32,* 67-89.

Pälike, H. et al. (2012), A Cenozoic record of the equatorial Pacific carbonate compensation depth, *Nature, 488,* 609-614, doi: 10.1038/nature11360.

Pogge von Strandmann, P. A. E., and G. M. Henderson (2015), The Li isotope response to mountain uplift, *Geology*, *43*, 67-70, doi: 10.1130/G36162.1.

Rowley, D. B. (2002), Rate of plate creation and destruction: 180 Ma to present, *Geol. Soc. Am. Bull.*, *114*, 927-233.

Sharp, W. D., and D. A. Clague (2006), 50-Ma initiation of Hawaiian-Emperor Bend records major change in Pacific plate motion, *Science, 313*, 1281-1284, doi: 10.1126/science.1128489.

Stallard, R. F., and J. M. Edmond (1981), Geochemistry of the Amazon: Part I. Precipitation chemistry and the marine contribution to the dissolved load at the time of peak discharge, *J. Geophys. Res., 86*, 9,844-9858.

Stallard, R. F., and J. M. Edmond (1983), Geochemistry of the Amazon: Part 2. The influence of geology and weathering environment on the dissolved load, *J. Geophys. Res.*, *88*, 9,671- 9,688.

Stallard, R. F., and J. M. Edmond (1987), Geochemistry of the Amazon: Part 3. Weathering chemistry and limits to dissolved inputs, *J. Geophys. Res., 92,* 8, 293-8302.

Stanley, S. M., L. A. Hardie (1999), Hypercalcification: Paleontology links plate tectonics and geochemistry to sedimentology, *GSA Today*, *9,* 1-7.

Tappert, R., R. C. McKellar, A. P. Wolfe, M. C. Tappert, J. Ortega-Blanco, and K. Muehlenbachs (2013), Stable carbon isotopes of C-3 plant resins and ambers record changes in atmospheric oxygen since the Triassic, *Geochim. Cosmochim. Acta*, *121*, 240- 262.

Veizer, J., and J. Hoefs (1976), The nature of O^{18}/O^{16} and C^{13}/C^{12} secular trends in sedimentary carbonate rocks, *Geochim., Cosmochim. Acta, 40,* 1387-1395.

Walker, J. C. G., P. B. Hays, and J. F. Kasting (1981), A negative feedback mechanism for the long-term stabilization of Earth's surface temperature, *J. Geophys. Res.*, *86*, 9,776-9,782.

Wang Y, T. E. Cerling, and B. J. MacFadden (1994), Fossil horses and carbon isotopes: new evidence for Cenozoic dietary, habitat, and ecosystem changes in North America, *Palaeogeog. Palaeoclim. Palaeoecol.*, *107*, 269-279.

Wortmann, U. G., and A. Paytan (2012), Rapid variability of seawater chemistry over the past 130 million years, *Science*, *337*, 334-336.

Zachos, J. C., G. R. Dickens, and R. E. Zeebe (2008), An early Cenozoic perspective on greenhouse warming and carbon-cycle dynamics, *Nature*, *451*, 279-283.

Chapter 9

Glaciers Fluctuate

Over the last 50 million years the Earth's polar regions have steadily cooled. We know this because the ^{18}O record kept by benthic foraminifera. It tells us that the deep ocean temperature dropped by about 10°C during this time interval. Today seawater with a temperature close to its freezing point cascades down the margin of the Antarctic continent into the abyss. Somewhere along the way the Antarctic ice cap nucleated. It now covers the entire continent. The snow which falls in its interior lithifies and flows slowly toward the continent's margins. Its fate is to calve into the ocean. This flow is driven by the weight of a three-kilometer-thick ice sheet warmed from beneath by geothermal heat. The creation of this huge edifice lowered sea level by about 60 meters.

The north polar region was spared extensive ice cover until about two and a half million years ago. Then ice sheets formed in North America and Europe. But, unlike their Antarctic cousin, these ice sheets oscillated in size causing the level of the sea to go up and down by as much as 120 meters. By contrast, during this time, the size of the Antarctic ice sheet remained largely unchanged. Further, the small fluctuations in its size which did occur were likely driven by changes in sea level associated with the waxing and waning of the northern ice sheets.

It is this waxing and waning with which this chapter is concerned. I contend that these large fluctuations in size were driven mainly by changes in the CO_2 content of the atmosphere. During the last half million years, CO_2 has gone up and down ranging from highs of about 280 parts per million to lows of about 190 parts per million (Fig. 9- 1). During the CO_2 lows, the Northern Hemisphere ice sheets achieved their maximum size. During the CO_2 highs, they largely disappeared.

There are two schools of thought regarding what drove the shifts in atmosphere's CO_2 content. The traditional one is that they involved the uptake and release of CO_2 by the

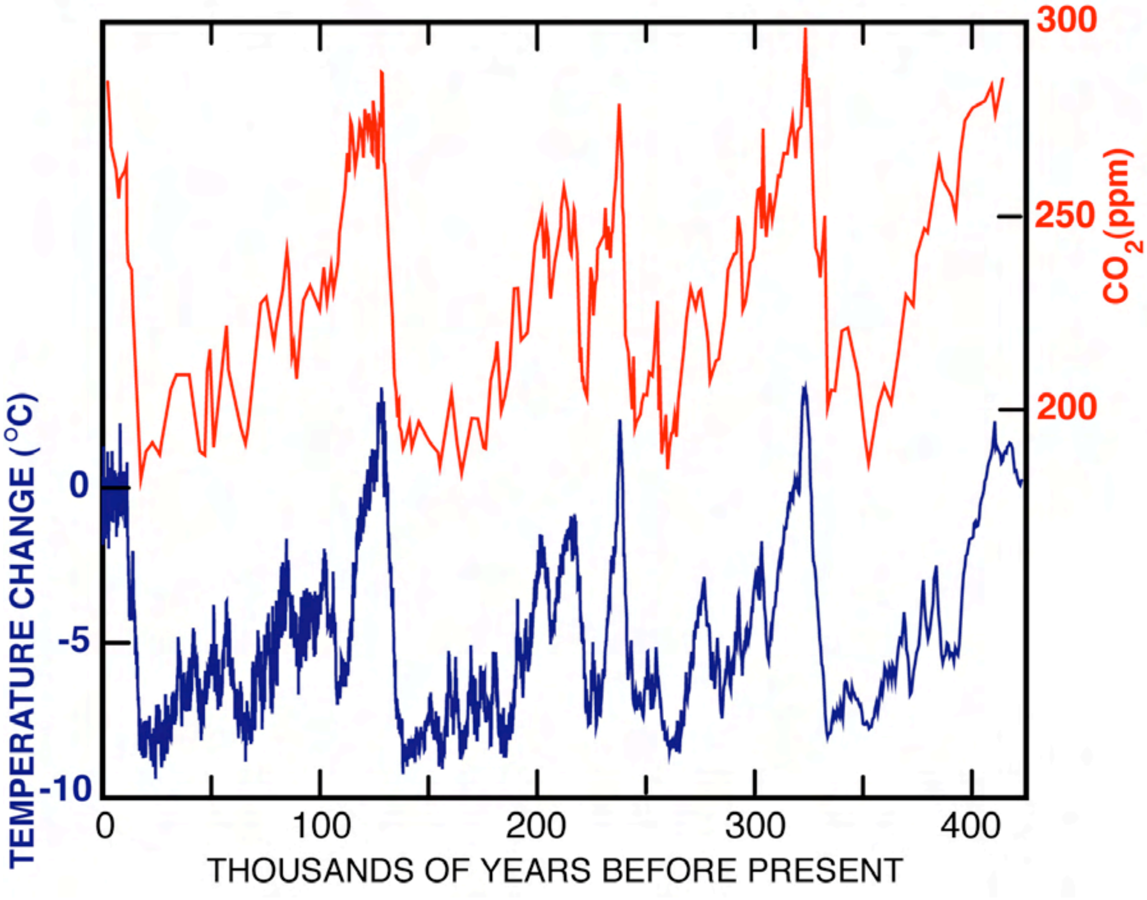


Figure 9-1. Records of CO_2 and air temperature for the last 400,000 years from an ice core drilled by Russian scientists at the Vostok Camp site on the Antarctica polar plateau. The CO_2 record generated by Jerome Chappellaz is based on measurements on air trapped in bubbles in the ice. The temperature record is derived from deuterium to hydrogen ratios measured by Jean Jouzel in the ice itself. Both are French geochemists. As the air bubbles closed off at a depth of about 80 meters and the ice accumulates at only a few centimeters per year, a time offset of several thousand years separates these two records. In order to compare the timing of the two records, an adjustment must be made for the duration of this offset. As the magnitude of this adjustment remains uncertain, careful consideration must be given to the phasing of the CO_2 and temperature shifts.

ocean driven by changes in the extent to which the growth-limiting nutrient PO_4 is utilized by the organisms inhabiting the surface ocean. Recently, a second view has emerged. Harvard's Peter Huybers and Charles Langmuir propose that they were caused by pulsing of the release of CO_2 from our planet's interior. The idea is that the weight of glacial ice on volcanoes shut them down. Then when this ice melted and the weight was released, the volcanoes turned back on. The reason is that added ice load raised the melting point of mantle rock. Further, while pressure can be changed instantaneously, changes in temperature take far, far longer. As the production of $CaCO_3$ and organic residues is not limited by the availability of carbon, the rate of burial of carbon on the sea floor did not change significantly. This being the case, during the periods when volcanoes were shutdown, the ocean-atmosphere inventory of CO_2 was drawn down. As the evidence in support of each of these hypotheses is reasonably strong, both likely played a role in the atmosphere's CO_2 changes. Uptake of atmospheric CO_2 by the ocean would cause the ice sheets and mountain glaciers to grow. The weight of the extra ice would squelch CO_2 release and hence serve to amplify the ocean's drawdown of CO_2.

Lacking a knowledge of essential details regarding either of these sources of CO_2 drawdown, the distinction between them must be based on less direct evidence. Before discussing this evidence, it must be pointed out that it is widely accepted that changes in the seasonality of insolation created by cyclic changes in the Earth's orbit somehow paced the growth and retreat of the Northern Hemisphere ice sheets. The basis for this conclusion is that there is a very close tie between the timing of seasonality changes and ice sheet fluctuations. Two scenarios regarding the nature of this link between insolation seasonality and glaciation are on the table. Traditionally scientists have thought in terms of the impact of summer insolation on the size of the Northern Hemisphere's large ice sheets. As made clear by the sea level record, at least on a 20-kyr timescale, the size of these ice sheets has tracked summer insolation. This fits with the conclusion reached by those who model today's glaciers that summer melting dominates their mass balance.

The problem with this scenario is that mountain glaciers at temperate latitudes in both hemispheres stood at their maximum extent between 25 and 18 thousand years ago (Fig. 9-2). This has now been documented by hundreds of ^{14}C and ^{10}Be ages for moraines in the Southern Hemisphere's Chilean Andes and New Zealand Alps, and in the Northern Hemisphere's Wind River and Sierra Nevada mountains. The same is the case for the North American ice sheet. Again, both ^{14}C and ^{10}Be age document that it reached its maximum extent along both its eastern and southern margins close to 22 kyrs ago. Further, sea level reached its lowest point about 22 kyrs ago (Fig. 9-3). At this time Northern Hemisphere summer insolation was at a minimum. But that for the Southern Hemisphere was at a maximum. This antiphasing of summer insolation on a 20-kyr time scale is related to the precession of the Earth's spin axis.

The obvious way to explain this hemispheric symmetry in glacial response is to call on CO_2 rather than summer insolation as the primary driver. If so, then the question becomes what sets the atmosphere's CO_2 content? In my book entitled "What Drives Glacial Cycles?" I propose that changes in seasonality provoke reorganizations of the ocean's large-scale thermohaline circulation. Presumably they do this by altering the high latitude fresh water budgets and hence the density of surface ocean waters in the polar regions. If my hypothesis is correct, then the chain of causality is as follows: seasonality cycles drive ocean circulation, ocean circulation drives CO_2, CO_2 drives mountain glaciation, and mountain glaciers perturbs the delivery of volcanic CO_2 (Fig. 9-4).

The key to drawing CO_2 into and out of the ocean is the alteration in the extent to which the PO_4, the limiting algal nutrient, is utilized. The focus is on the Southern Ocean. Today only about one third of the PO_4 upwelled into this partially ice-covered and often dark ocean is sent back into the interior fixed into organic matter. The rest returns to the interior in dissolved form. If two thirds, rather than one third, of these nutrients were to be utilized, the CO_2 partial pressure in Southern Ocean surface water would drop to its glacial level (i.e., from 280 to 190 μatm). Although the Southern Ocean constitutes only 15 percent

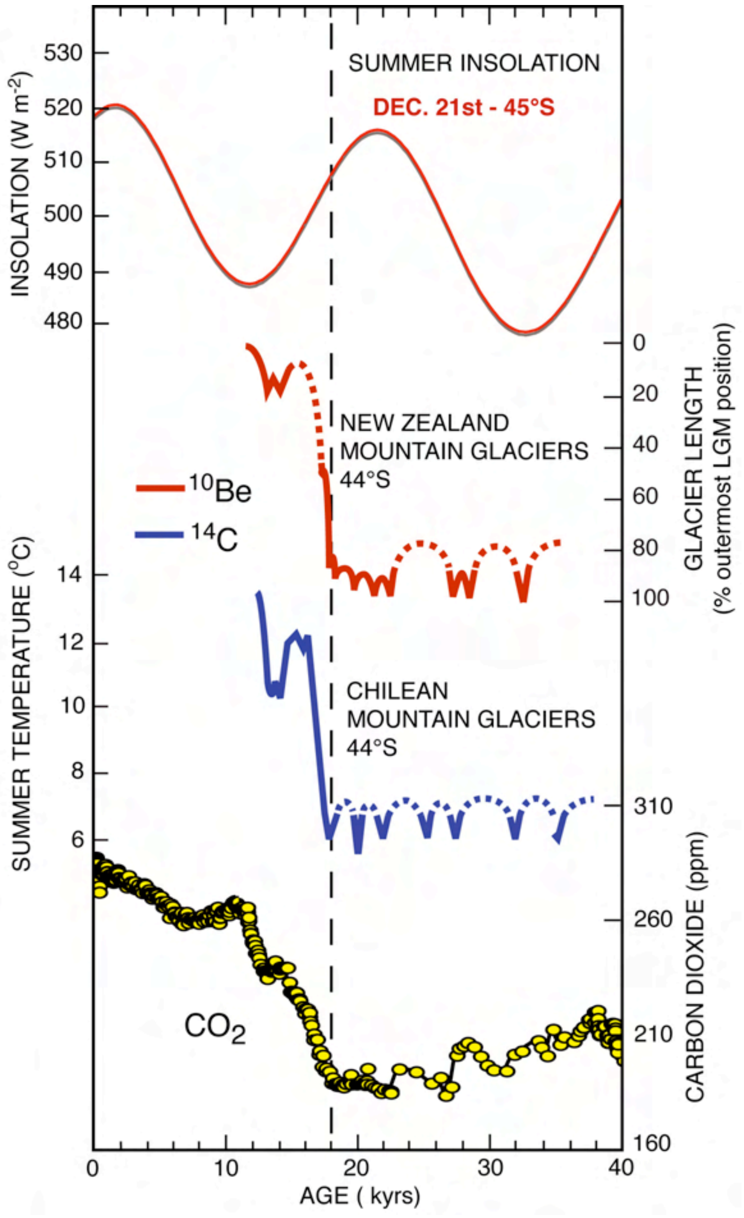


Figure 9-2. The record provided by moraines in New Zealand's Alps and in Chile's Andes points to CO_2 rather than summer insolation as the primary driver of glacial extent. Were the latter in control, then these glaciers should have been smaller 22 kyrs ago than they were 32 kyrs ago. Instead, they remained near their maximum extent from at least 35 kyrs to 18 kyrs ago. Then at the same time CO_2 began its post-glacial rise, these glaciers commenced a rapid retreat. Note the agreement between the New Zealand chronology which is based on ^{10}Be measurements on quartz contained in large boulders and the Chilean chronology which is based on ^{14}C measurements on wood and peat from above, within, and below glacial tills.

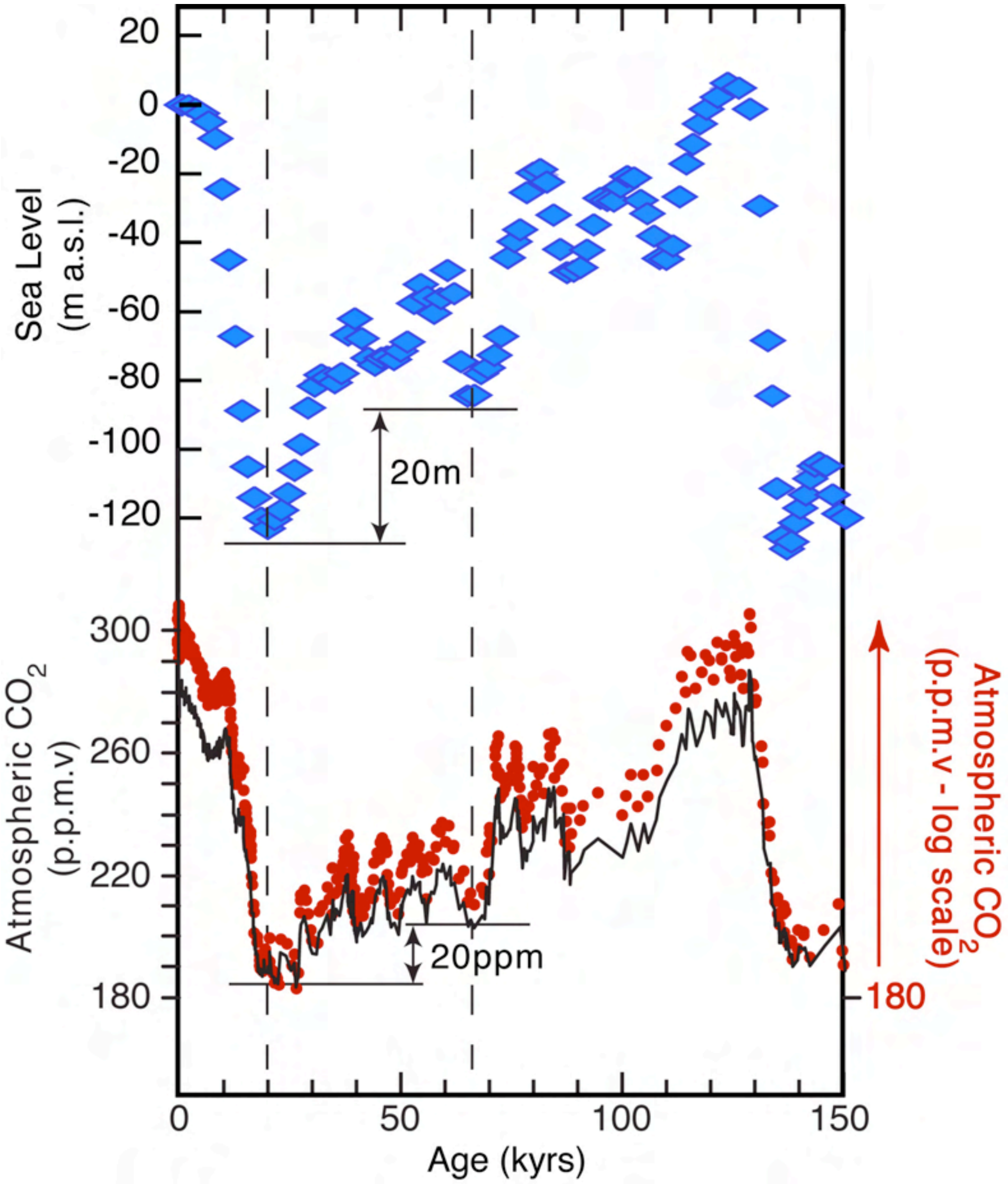


Figure 9-3. Comparison of the sea level and atmospheric CO_2 records for the last glacial cycle. Although for the last half of the cycle the two have quite similar shapes, for the first half, two differences stand out: 1) the initial drop in sea level precedes that of CO_2 and 2) sea level peaked three times (at 124, 103 and 82 kyrs), but CO_2 only twice. As the temperature response to CO_2 is logarithmic rather than linear, the CO_2 record is plotted on a logarithmic scale (red dots). As can be seen from the linear plot (black line), this makes only a small difference.

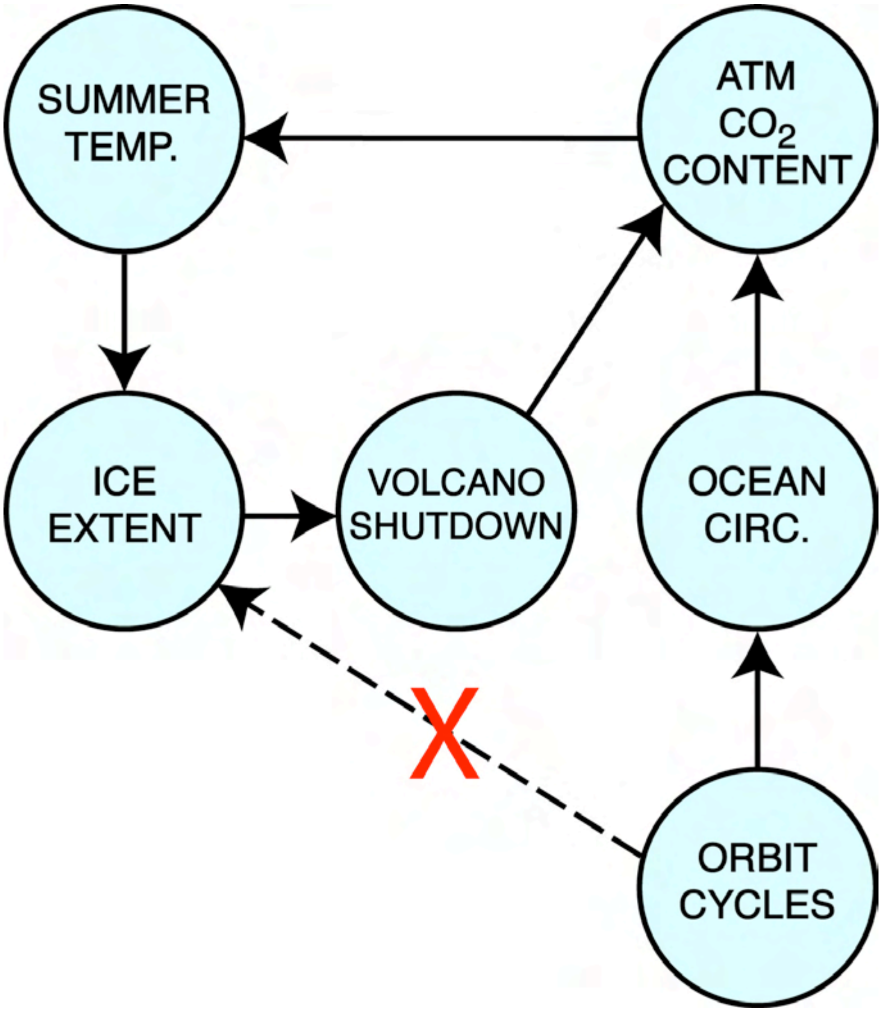


Figure 9-4. Causal chain coupling orbital-induced seasonality cycles to ice extent. Instead of a direct link to summer insolation, I suggest that changes in the freshwater input in the regions of the oceans where deep water forms led to reorganizations of the ocean's thermohaline circulation. This, in turn, led to uptake and release of CO_2 from the oceans. These CO_2 changes drive the planets glaciers and ice sheets. Finally, the weight of the extra ice reduces volcanic activity, cutting down the CO_2 input to the atmosphere-ocean reservoir and in this way supplementing the drawdown of CO_2.

of the surface ocean, it has a disproportionate influence on the atmosphere's CO_2 content. The reason is that models show that CO_2 transfer through the atmosphere from one part of the surface ocean to another tends to pull the pCO_2 in the rest of the surface ocean toward that in the Southern Ocean.

Ever since 1980 when Swiss and French scientists first documented that the air trapped in bubbles of glacial-age polar ice had lower CO_2 contents than the bubbles in Holocene ice, the growth-limiting nutrient PO_4 has held center stage. The initial idea was that the ocean inventory of PO_4 was larger during peak glacial time than during peak interglacial time. In this case, the reduction of CO_2 would not require a change in utilization efficiency. Increasing the glacial ocean's phosphate inventory was an obvious way to strengthen the ocean's so-called biological pump. Plants fix CO_2 in surface waters. Some of the organic matter created in this way finds its way into the ocean's interior where it is 'eaten', releasing CO_2. In this way, organisms pump CO_2 from the surface into the ocean's interior.

When a decade later, it was suggested that the atmosphere's CO_2 content was dictated by that in the surface waters in the Southern Ocean, emphasis shifted toward what controlled the extent of utilization of its upwelled phosphate (Fig. 9-5). This line of thinking received a huge boost when John Martin demonstrated that the element iron essential to the manufacture of many essential enzymes was in short supply. Iron is the least soluble element. It is removed from the water by absorption onto particulate matter in just a few weeks after reaching the ocean. Martin showed that, given more iron, the nutrient PO_4 was more efficiently utilized. Much of the ocean's iron supply is derived from dust blown off the continents. Because of its isolation from continental dust sources, the Southern Ocean receives very little iron. So, Martin proposed that higher utilization of Sothern Ocean nutrients during glacial time could have been driven by a larger input of dust.

His thinking was subsequently supported by the dust record contained in Antarctic ice. The rain rate was far higher during times of peak glaciation than during times of interglaciation. So, iron fertilization fits well with the scenario that a greater efficiency in

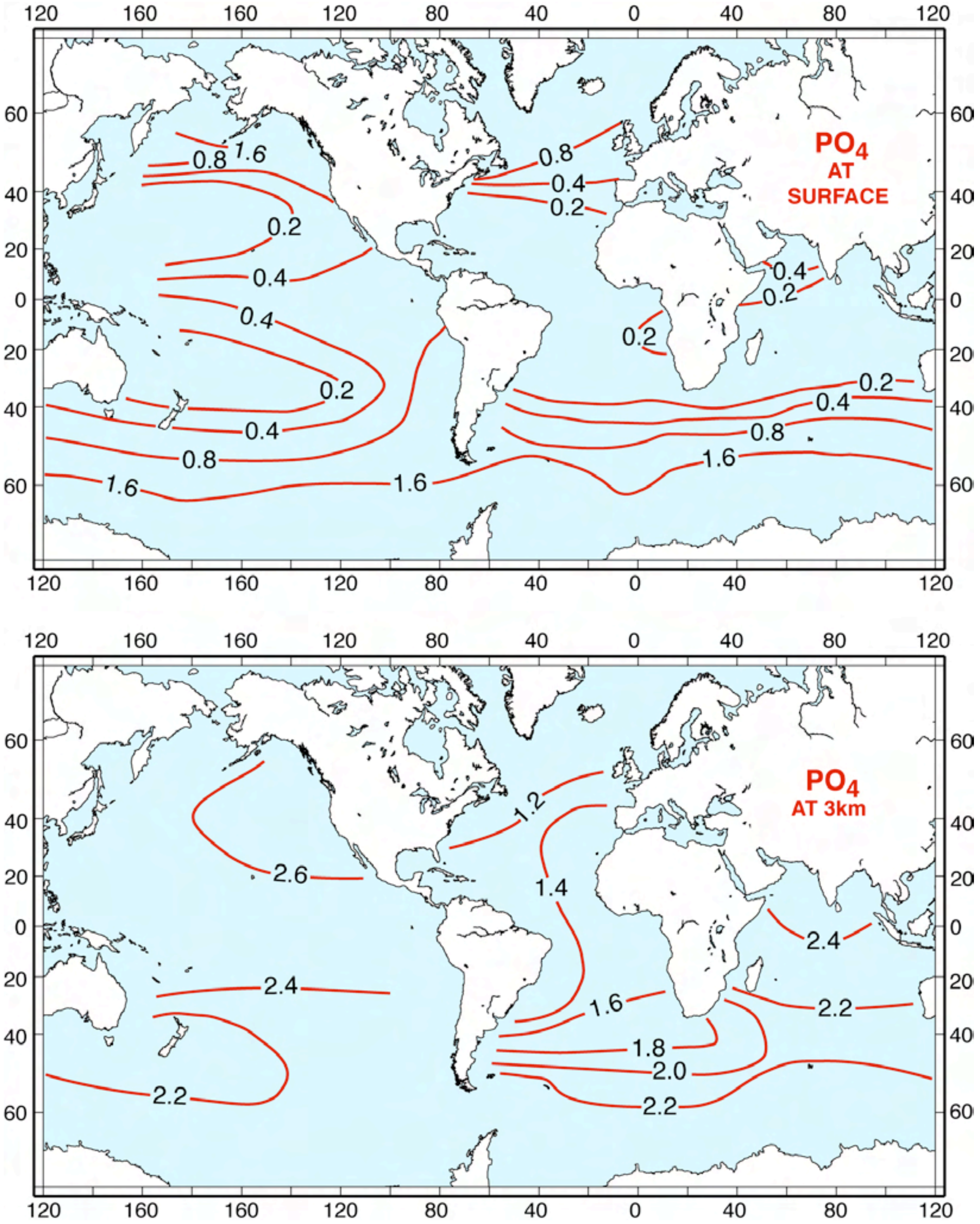


Figure 9-5. The distribution of PO_4 in today's ocean. The upper panel is for surface waters and the lower panel for water at 3-km depth. As can be seen, waters at the surface of the Southern Ocean contain more PO_4 than any others. Deep water containing about 2.2 μmol PO_4 per liter is upwelled to the surface of the Southern Ocean where about 0.6 μmol PO_4 per liter is utilized by algae. The remaining 1.6 μmol per liter escapes utilization. More efficient utilization of this PO_4 is the favored explanation for the glacial drawdown of atmospheric CO_2.

the utilization of phosphate upwelled in the Southern Ocean was responsible for the lowering of the atmosphere's CO_2 content during glacial time. As shown by Princeton's Danny Sigman, measurements of the isotopic composition on nitrogen trapped in opaline frustules produced by diatoms lend support to John Martin's hypothesis that the PO_4 upwelled into the glacial Southern Ocean was more efficiently utilized than it is today. Nitrogen isotopes provide a measure of utilization because isotopically light $^{14}NO_3^-$ is utilized in slight preference to isotopically heavy $^{15}NO_3^-$. This being the case, the greater the extent of utilization the higher the ^{15}N to ^{14}N ratio becomes in the unused nitrate. Sigman found that in that portion of the Southern Ocean closest to Antarctica, the $\delta^{15}N$ in nitrogen trapped in opaline diatom tests was higher during the last glacial maximum than during the Holocene.

But if this is the case, my scenario regarding the link between insolation cycles and glaciation is in trouble. The reason is that, as championed by MIT's David McGee, dustiness is driven by atmospheric gustiness and gustiness is tied to latitudinal temperature gradient. During peak glacial time, polar temperatures dropped by more than 10°C, but tropical temperatures dropped by only about 3°C. Records in all parts of the globe document that during peak glacial time the dust rain was at least twice that for the Holocene. For the Greenland and Antarctic ice caps, it was more like tenfold higher. The larger pole to equator temperature gradient presumably led to an increase in the frequency of cyclonic storms capable of entraining dust. If so, the polar cooling must be the cause of enhanced iron delivery to the Southern Ocean. But, if this is the case, the cooling must have preceded the CO_2 decline. One might say the cart got ahead of the horse.

Although the dust record matches many of the features of the CO_2 record, there is one glaring difference (Fig. 9-6). Its rain does not increase significantly at the time of the initial drop in atmospheric CO_2 content (at 115 kyrs) which followed the last interglacial maximum. It accounts for about half of the 90 ppm glacial reduction. I would like to think that iron fertilization serves as an amplifier rather than as the primary driver for ocean productivity changes. If so, something else must have generated the more efficient use of Southern

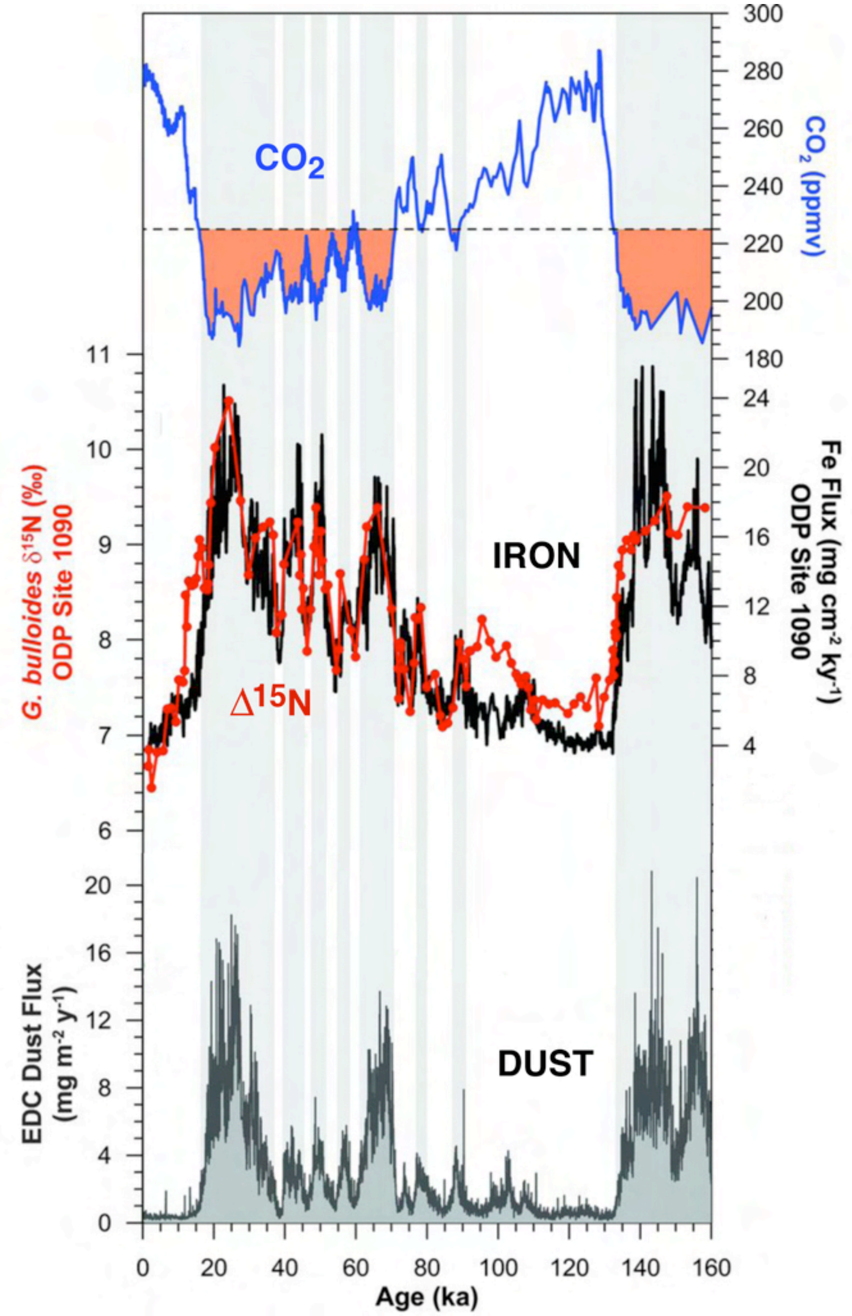


Figure 9-6. Comparison of an Antarctic ice cap dust flux record with a Southern ocean iron flux record. That the extra glacial iron enhanced the utilization of phosphorus is indicated by the strong correlation with the nitrogen isotope record for trace amounts of organic matter contained in planktonic foraminifera *G. bulloides*. Increases in ^{15}N signify increases in PO_4 utilization (see text). Although imperfect, the nitrogen isotope record anti-correlates with the nitrogen isotope record (Martinez-Garcia, 2014).

Ocean phosphate 115 kyrs ago. Identifying the ‘something else’ has proven elusive. The most spoken of idea is that the deep ocean was more strongly stratified during peak glacial time than it is today. Evidence for this comes from the deep Atlantic. Today, except for the thin wedge of Antarctic Bottom Water, its phosphate concentration is nearly constant with depth. But during glacial time this was not the case. The $\delta^{13}C$ and the cadmium content of foraminifera shells serve as proxies for the distribution of phosphate. Both proxies tell us that during peak glacial time there was a major difference in the phosphate profile in the deep Atlantic. The water below this 25 km depth had a higher PO_4 content than today’s and that above this level a lower PO_4 content.

In order to explain this it is tempting to postulate that during glacial time today’s thin wedge of Antarctic Bottom Water was much thicker. But whereas today’s Antarctic Bottom Water has exactly the same phosphate content as that for the deep water entering the abyssal Pacific, this was not the case during glacial time. Although its phosphate content shifted toward that for the deep glacial Pacific, it did not shift all the way. The $\delta^{13}C$ for deep water in both the Atlantic and Pacific shifted to lower values than those for the Holocene (Fig. 9-7). But were the PO_4 content of abyssal Atlantic to have been the same as that in the Pacific, the decrease in $\delta^{13}C$ in the Pacific would have to have been 1.3 per mil larger than that for the Atlantic. But, as recorded by benthic foraminifera, the actual shift in the Pacific was only 0.4 ± 0.1 per mil. Hence the mode of formation of glacial- age abyssal Atlantic water could not have been the same as that for today’s Antarctic Bottom Water. Further, only one mixture can be generated in the deep Southern Ocean. The reason is that waters entering the deep Southern Ocean from the Atlantic and descending from the surface are totally homogenized in a single pass around the Antarctic continent. Hence a sizable fraction of the glacial-age abyssal Atlantic water must have been created elsewhere. One possible scenario is that it forms beneath sea ice in the northern Atlantic (Fig. 9-8).

Making matters more interesting, the composition of both the upper and lower deep Atlantic water masses changed during the course of the last glacial cycle (Fig. 9-9).

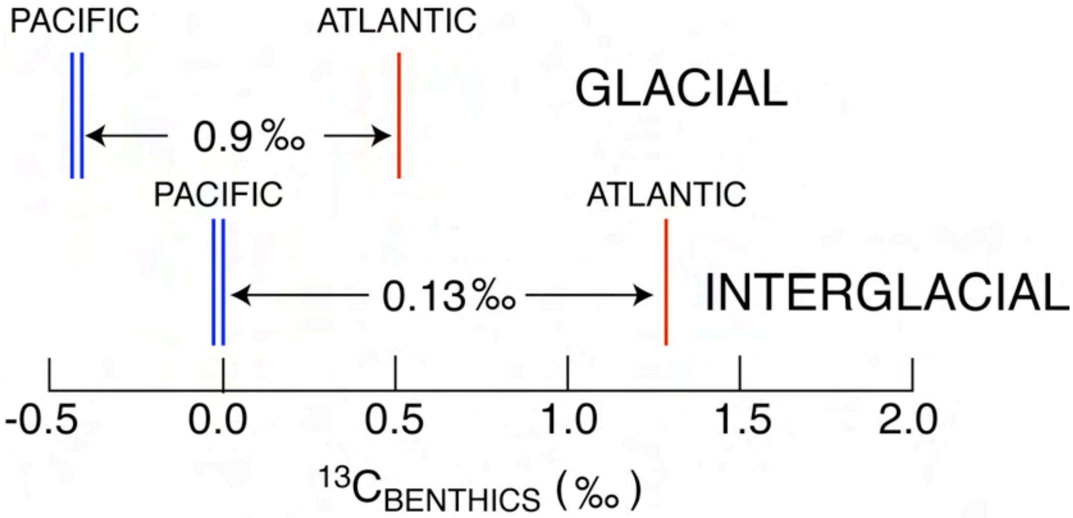


Figure 9-7. In today's ocean, the $\delta^{13}C$ in the deep Atlantic is about 0.13 per mil higher than that in the deep Pacific. During glacial time, the record kept in benthic foraminifera shells shows that the $\delta^{13}C$ in both became more negative. Although the difference decreased, it remained quite large.

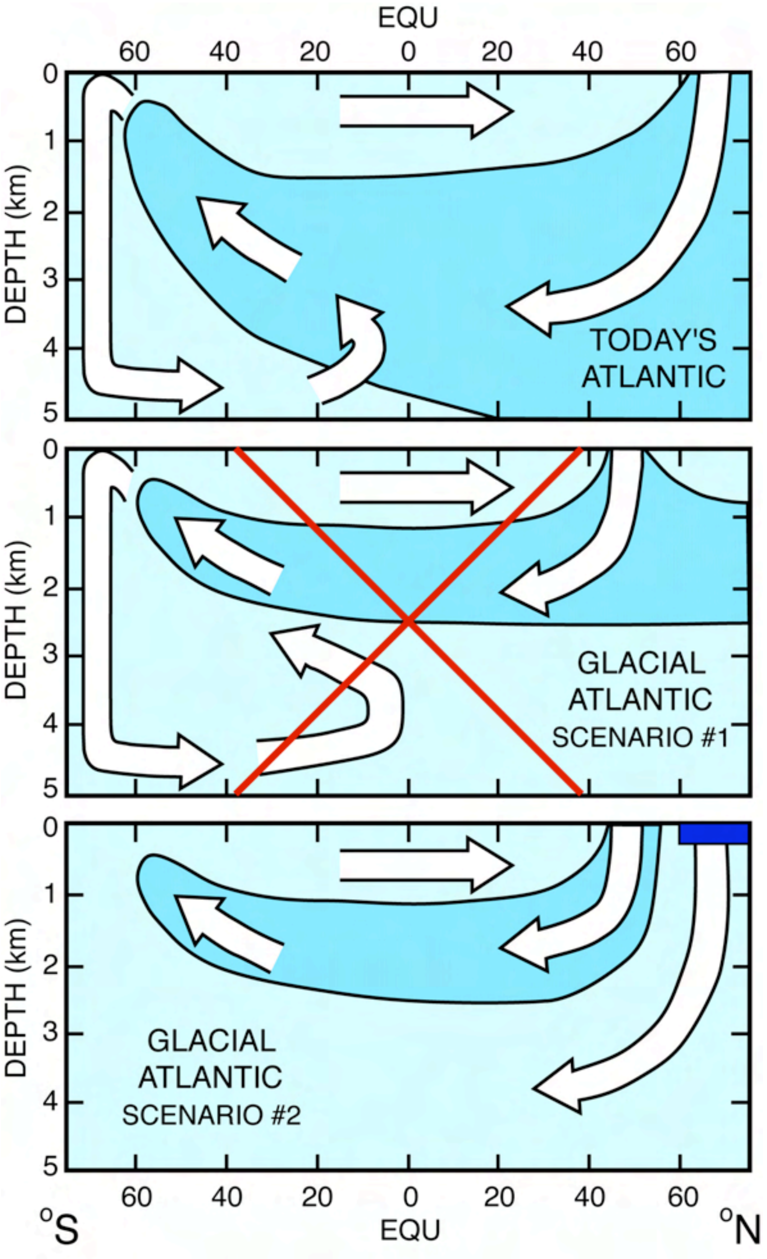


Figure 9-8. Contrast between the water mass structure in today's deep Atlantic and the Atlantic during the time of peak glaciation (i.e., 25 to 18 kyrs). Today deep water produced in the northern Atlantic floods nearly its entire deep basin. Except in the thin wedge of Antarctic Bottom Water entering from the south, the phosphate content is uniform with depth. By contrast, during peak glacial time, the deep Atlantic was nutrient stratified. The water above 2.8 km had a lower phosphate content and the water below this depth a higher phosphate content than today. I suspect that the water below 2.8 km formed beneath sea ice and that above 2.8 km in the open Atlantic south of the ice front. The composition of both deep water types has varied with time but in opposite senses.

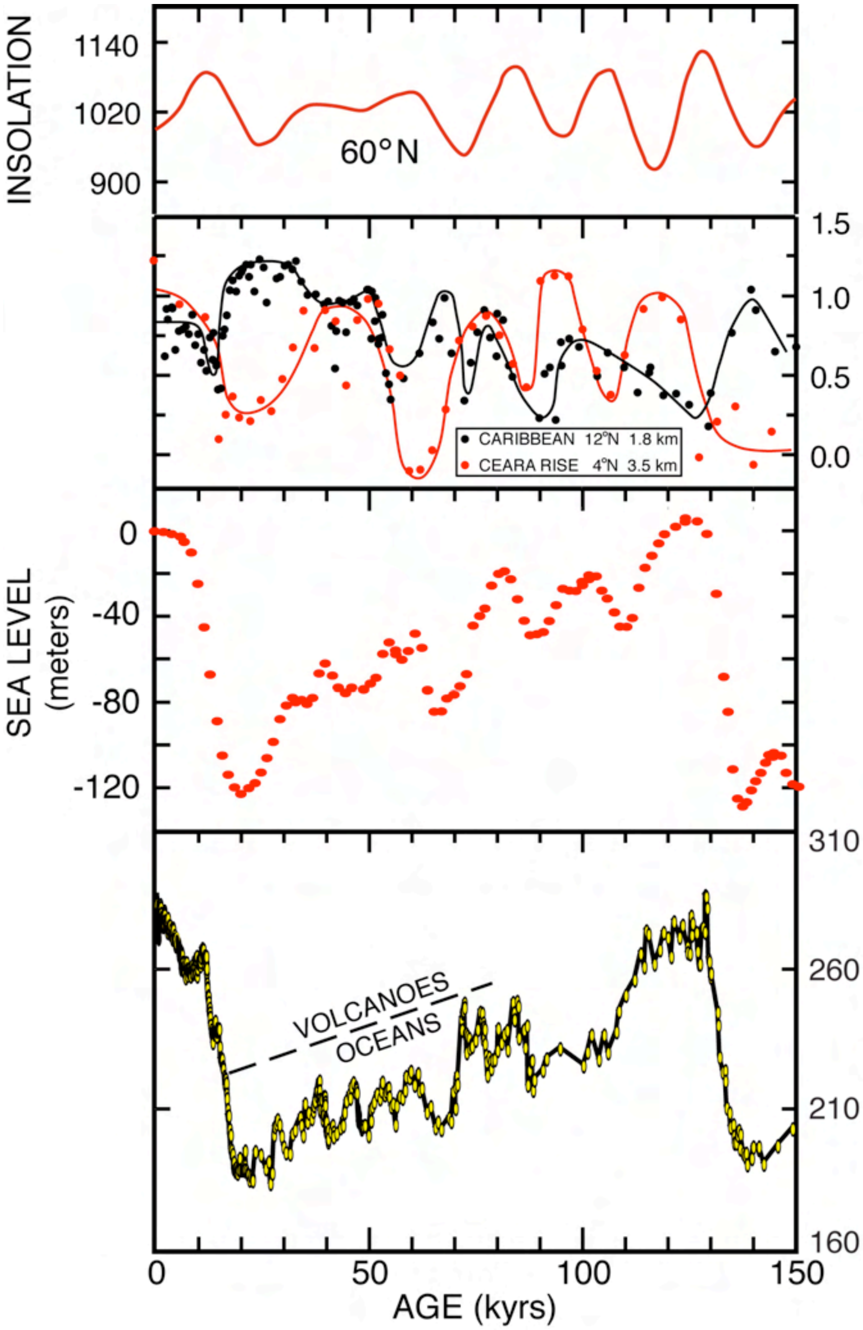


Figure 9-9. Shown here is the δ^{13}C record for two sediment cores. The one from the Caribbean (black dots) is representative of upper Atlantic deep water and that from the Ceara Rise water from lower Atlantic deep water. Note that they are 'flat' showing 20-kyr fluctuations but none of the ramp-like character of the CO_2 record. This led me to propose that the ramp-like decline is the result of the reduction of volcanic activity, and the fluctuations around this descending ramp are the result of uptake and release of CO_2 by the ocean.

And these changes were in the opposite sense. The larger the drop in $\delta^{13}C$ in the abyssal water mass the larger the positive rise in the upper deep water. I would like to think that the extent of divergence serves as a proxy for the strength of deep ocean stratification and hence also of the extent of CO_2 uptake by the ocean. This leads me to propose that the downward ramp in CO_2 content was not the result of progressively greater ocean uptake. Rather, it was the result of a reduction in the supply of CO_2 from the planet's interior. The role of ocean uptake was instead to modulate this downward trend. Were the ramp removed, the atmosphere's CO_2 record would be a better match to summer insolation in the Northern Hemisphere.

If the CO_2 missing from the glacial atmosphere were carried to the abyssal ocean as organic matter, then when oxidized, it would increase the ^{13}C deficiency in the dissolved inorganic carbon. Indeed, glacial-age benthic forams have lower $\delta^{13}C$ values than their Holocene counterparts. For the deep Pacific, this decrease averaged about 0.45 per mil and for the abyssal Atlantic about 0.70 per mil. I say 'abyssal' because almost all of the available measurements have been made on open ocean sediments rather than continental margin sediments. This being the case, as the depth of the ridge crests is about 2.5 km, measurements have been made on only a limited number of sediments from shallower depths. Assuming that the $\delta^{13}C$ change for the abyssal Indian Ocean is similar to that for the Pacific, the average for the entire abyssal ocean is about 0.5‰.

The volume of the ocean beneath 2.5 km is about one third that for the entire ocean In today's ocean, for every additional μmol/liter of PO_4 added by the decomposition of organic matter, the $\delta^{13}C$ drops by about one per mil. The C to P ratio in marine organic matter averages 125. If the same was true for the glacial ocean, then for each 0.1‰ decrease in $\delta^{13}C$ would correspond to the addition of about 50 gigatons of carbon as respiration CO_2. In order to account for the entire 150 gigatons of carbon missing from the glacial atmosphere, the drop in $\delta^{13}C$ would have to be only about 0.3 per mil. And if half of the CO_2 drawdown were attributed to the shutdown of volcanic emissions, then the required amount would be only about 75 gigatons of carbon. But in order to reduce the atmosphere's

CO_2 content would require a reduction in the upper ocean DIC.

But, complicating matters, is a second contribution to $\delta^{13}C$ reduction. It has to do with the loss of terrestrial biomass during glacial time. For each 125 gigatons of terrestrial carbon lost, there would be 0.1‰ decrease in the $\delta^{13}C$ of ocean carbon. Assuming that the loss of biomass was primarily from those parts of the boreal forests covered with glacial ice or permafrost, the amount lost would be on the order of 250 gigatons C. This would have caused the whole ocean $\delta^{13}C$ to drop by about 0.2 per mil. If so, the amount attributable to storage of excess respiration CO_2 in the deep sea would be 0.3‰ or about 150 gigatons of carbon. It should be mentioned that storing more respiration CO_2 in the deep ocean does not require a larger phosphate inventory in the glacial ocean. Rather, the phosphate accompanying the extra respiration CO_2 could easily be supplied by converting unutilized PO_4 into utilized PO_4.

But the change in tropical biomass must also be taken into account. It has been proposed that during peak glacial time the tropics had less rainfall and as a consequence less forest biomass. However, the large continental shelf area in the Indonesian region exposed by the drop in sea level would likely have been forested adding biomass. So unfortunately, it is not possible to determine even the sign of the tropical contribution let alone its magnitude.

A problem with this approach is that it depends on the assumption that the storage of respiration CO_2 in two thirds of the ocean above 2.5 kilometers stayed the same as it is today. Clearly one could argue that the extra respiration CO_2 stored in the abyssal ocean was compensated by a decrease of the amount stored in the rest of the ocean. Indeed, there is a hint that it changed in the opposite direction. The Caribbean $\delta^{13}C$ record presented in Figure 9-9, while ambiguous in this regard, does suggest that at least for the last glacial maximum (22 kyrs ago), the $\delta^{13}C$ for upper layer of the deep water mass was a bit larger than during the Holocene. Unfortunately, there are as yet too few ^{13}C for benthic foraminifera from sites shallower than 2.5 km to even take a stab at estimating the magnitude of this compensation.

The idea that ice loading of volcanoes reduced the input of CO_2 to the ocean – atmosphere reservoir is not without its problems. The biggest one has to do with release of CO_2 from the basaltic lavas erupted at sea-floor spreading centers. This source is thought to be roughly equal to that from continental volcanoes. As the sea level drop associated with the buildup of ice on the continents reduces the pressure on the magma chambers beneath the ridge crests, one would expect this source to be out of phase with that associated with volcanoes. That mid-ocean ridge volcanism is impacted by glacial cycles is recorded in topographic profiles across ridge crests. The variations in elevation have the same frequencies as Milankovitch cycles. The hope of the proponents of this idea is that there is a delay in the expanse of magma injection which would bring the ocean floor contribution into phase with that for continental volcanoes. A work in progress.

Although we have a long way to go before either the ocean uptake of CO_2 or the reduction of CO_2 due to volcano shutdown can be fully understood, the evidence that CO_2 drove glaciation is clear. Taken together with the evidence from the PETM, it makes clear that the CO_2 we are adding to the atmosphere by fossil fuel burning will warm the planet.

References for Chapter 9

Abe-Ouchi, A.., F. Saito, K. Kawamura, M. E. Raymo, J. Okuno, K. Takahashi and H. Blatter (2013), Insolation-driven 100,000-year glacial cycles and hysteresis of ice-sheet volume, *Nature, 500,* 190-194.

Anderson, B., and A. Mackintosh (2006), Temperature change is the major driver of late-glacial and Holocene glacier fluctuations in New Zealand, *Geology*, *34*, 121-124, doi: 10.1130/G22151.1.

Anderson, R. F., S. Ali, L. I. Bradtmiller, S. H. H. Nielsen, M. Q. Fleisher, B. E. Anderson, and L. H. Burckle (2009), Wind-driven upwelling in the Southern Ocean and the deglacial rise in atmospheric CO_2, *Science*, *323*, 1443-1448.

Broecker, W., *What Drives Glacial Cycles*?, Eldigio Press, NY, 2013.

Broecker, W., and E. Clark (2001), A dramatic Atlantic dissolution event at the onset of the last glaciation, *Geochem. Geophys. Geosyst., 2,* art. no. –2001GC000185.

Denton, G. H., C. J. Heusser, T. V. Lowell, C. Schlüchter, B. G. Andersen, L. E. Heusser,, P .I. Moreno, and D. R. Marchan (1999), Geomorphology, stratigraphy, and radiocarbon chronology of Llanquihue drift in the area of the southern Lake District, Seno Reloncavi, and Isla Grande de Chiloé, Chile, *Geografiska Annaler, 81A,* 167-229.

Hays, J. D., J. Imbrie, and N. J. Shackleton (1976), Variations in Earth's orbit – pacemaker of ice ages, *Science 194*, 1121-1132.

Huybers, P., and C. Langmuir (2009), Feedback between deglaciation, volcanism, and atmospheric CO_2, *Earth Planet. Sci. Letts.*, *286*, 479-491, doi: 10.1016/j.epsl.2009.07.014.

Jaccard, S. L., C. T. Hayes, A. Martínez-Garcia, D. A. Hodell, R. F. Anderson, D. M. Sigman, and G. H. Haug (2013), Two modes of change in Southern Ocean productivity over the past million years, *Science*, *339*, 1419-1423.

Kelly, M. A., J. M. Russell, M. B. Baber, J. A. Howley, S. E. Loomie, S. Zimmerman, B. Nakileza, and J. Lukaye (2014), Expanded glaciers during a dry and cold Last Glacial Maximum in equatorial East Africa, *Geology*, Data Repository item 2014184/doi: 10.1130/G35421.1.

Lisiecki, L., E., and M. E. Raymo (2013), A Pliocene-Pleistocene stack of 57 globally distributed benthic $\delta^{18}O$ records, *Paleoceanography*, *20,* PA1003, doi:10.1029/2004PA001071.

McGee, D., W. S. Broecker, and G. Winckler, (2010), Gustiness: The driver of glacial dustiness?, *Quat. Sci. Rev., 29,* 2340-2350, doi: 10.1016/j.quascirev.2010.06.009.

Martin, J. (1990), Glacial-interglacial CO_2 change: The Iron Hypothesis, *Paleoceanography, 5*, 1-13.

Martínez-Garcia, A., D. M. Sigman, H. Ren, R. F. Anderson, M. Straub, D. A. Hodell, S. L. Jaccard, T. I. Eglinton, and G. H. Haug (2014), Iron fertilization of the Subantarctic Ocean during the last ice age, *Science*, *343*, 1347-1350.

Mercer, J. H. (1972), Chilean glacial chronology 20,000 to 11,000 carbon-14 years ago: Some global comparisons, *Science*, *176*, 1118-1120.

Monnin, E., A. Indermühle, A. Dällenbach, J. Flückiger, B.Stauffer, T. F. Stocker, D. Raynaud, and J.-M. Barnola. (2001), Atmospheric CO_2 concentrations over the Last Glacial Termination, *Science, 291*, 112-114.

Petit, J. R., et al., (1999), Climate and atmospheric history of the last 420,000 years from the Vostok ice core, Antarctica, *Nature*, *399*, 429-437, doi:10.1038/20859.

Pogge von Strandmann, P. A. E., and G. M. Henderson (2015), The Li isotope response to mountain uplift, *Geology*, *43*, 67-70, doi: 10.1130/G36162.1.

Putnam, A. E., J. M. Schaefer, G. H. Denton, D. J. A. Barrell, S. D. Birkel, B. G. Andersen, M. R. Kaplan, and R. C. Finkel, (2013), The Last Glacial Maximum at 44°S documented by a ^{10}Be moraine chronology at Lake Ohau, Southern Alps of New Zealand, *Quat. Sci. Rev., 62*, 114-141.

Yu, J. M. and H. Elderfield (2007), Benthic foraminiferal B/Ca ratios reflect deep water carbonate saturation state, *Earth Planet. Sci. Lett., 258,* 73-86, doi: 10.1016/j.epsl.2007.03.025.

Yu, J., G. L. Foster, H. Elderfield, W. S. Broecker, and E. Clark (2010), An evaluation of benthic foraminiferal B/Ca and delta(11)B for deep ocean carbonate ion and pH reconstructions, *Earth Planet. Sci. Lett., 293,* 114-120, doi: 10.1016/j.epsl.2010.02.029.

Chapter 10

Manmade CO_2

We are in the midst of manmade disruption of the carbon cycle. It involves the burning of fossil fuels. As of this writing, the CO_2 content of the atmosphere had reached 400 ppm, up 120 ppm from its pre-industrial content and is rising at the rate of 2.5 ppm per year. Further, as our fossil-fuel reserves are not about to run out, there is no end in sight.

In so doing, we are performing what the late Roger Revelle termed to be “man’s greatest geophysical experiment.” His choice of the word “experiment” is apt because we lack the means to make reliable predictions regarding any of its consequences. We know that it will warm the Earth, redistribute rainfall, melt ice, and enhance photosynthesis, but not by how much. Because of this large uncertainties loom with regard to the impact of these changes on food production, sea level and biodiversity. Claims are being made that it will up the frequency and strength of hurricanes, floods, droughts, insect infestations… Clearly it’s a very dangerous experiment. But as fossil fuels provide 85 percent of the world’s energy, the experiment will continue for decades to come. Further, its aftermath will be with us for hundreds of years.

Putting aside the potentially dire consequences, it is a fascinating experiment. This is especially true when taken together with another of our dangerous “experiments,” namely the testing of H-bombs. The radiocarbon generated by these tests serves as a very powerful tracer offering new insight into all aspects of the Earth’s carbon cycle. One might call the combination of these two experiments a repeat of the PETM for they involve the sudden addition of a large amount of CO_2 to our atmosphere accompanied by an isotopic companion capable of helping us to decipher its fate.

So far we have learned a number of important things about our Earth by monitoring fossil-fuel CO_2 and H-bomb ^{14}C. For example, since 1958 when precise monitoring of this greenhouse gas began, about 57 percent of the CO_2 we have generated has accumulated in the atmosphere. (Fig. 10-1). Further, roughly half of the remaining 43 percent has been taken up by the ocean (Fig. 10-2), and surprisingly, despite deforestation and agricultural manipulation of soils, the amount of carbon stored in our terrestrial biosphere has been steadily increasing. It accounts for the other half of the 43 percent. Ralph Keeling at UC San Diego, beautifully documented the fate of fossil fuel CO_2 by developing the means to measure the tiny decline in the atmosphere's O_2 content. He showed that the decline has been smaller than that expected from the burning of fossil fuels (Fig. 10-3). The only way to explain this is if more oxygen is being produced by plants than was being utilized to oxidize plant matter. For each extra carbon atom stored in the biosphere, one extra O_2 molecule is added to the atmosphere.

That the fraction of the CO_2 we produce which has remained in the atmosphere has not changed over the last half century is puzzling. We know that the surface ocean's capacity for CO_2 uptake should be steadily decreasing. The reason is that each CO_2 molecule taken up by the ocean mates with a $CO_3^=$ ion to form two HCO_3^- ions (Fig. 10-4). So, as $CO_3^=$ is consumed, the ocean's capacity to take up CO_2 correspondingly decreases. As the product of CO_2 and $CO_3^=$ concentrations in surface ocean remains nearly constant, each 10 percent rise in CO_2 produces roughly a 10 percent decline in $CO_3^=$. As the CO_2 content of the atmosphere has risen by almost 40 percent, were the surface ocean to have kept pace, its capacity should have dropped by about 40 percent. We know from CO_2 surveys in the surface ocean that the surface ocean is keeping pace with the atmosphere. The increase in CO_2 partial pressure rise in the surface ocean averages about 85 percent of that for the atmosphere.

A second aspect of ocean uptake has to do with the rate at which the extra CO_2 is mixed into the interior. The distribution of H-bomb ^{14}C (Fig. 10-5) in the ocean tells us that only about 15 percent of its capacity for CO_2 uptake has been tapped (Fig. 10-6). The distribution of natural radiocarbon in the ocean tells us that it will take hundreds of years before this capacity is fully utilized. The fraction of this capacity utilized depends on the

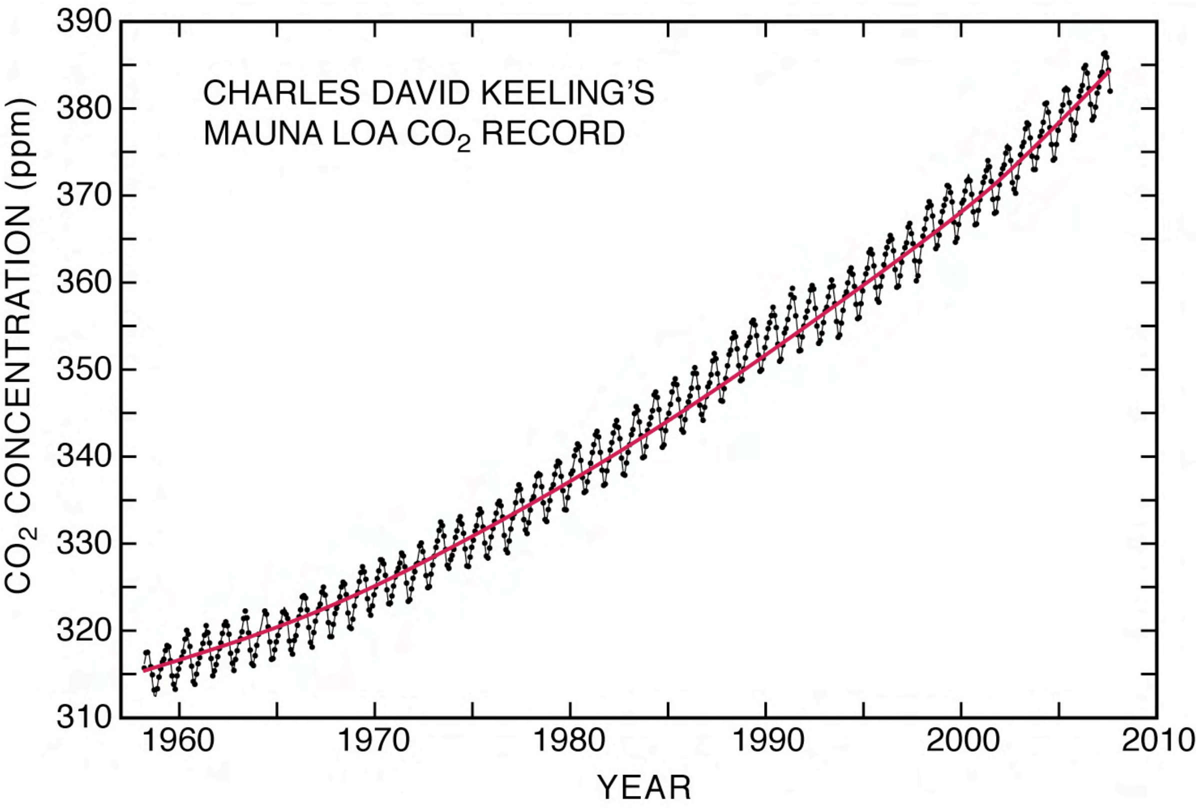
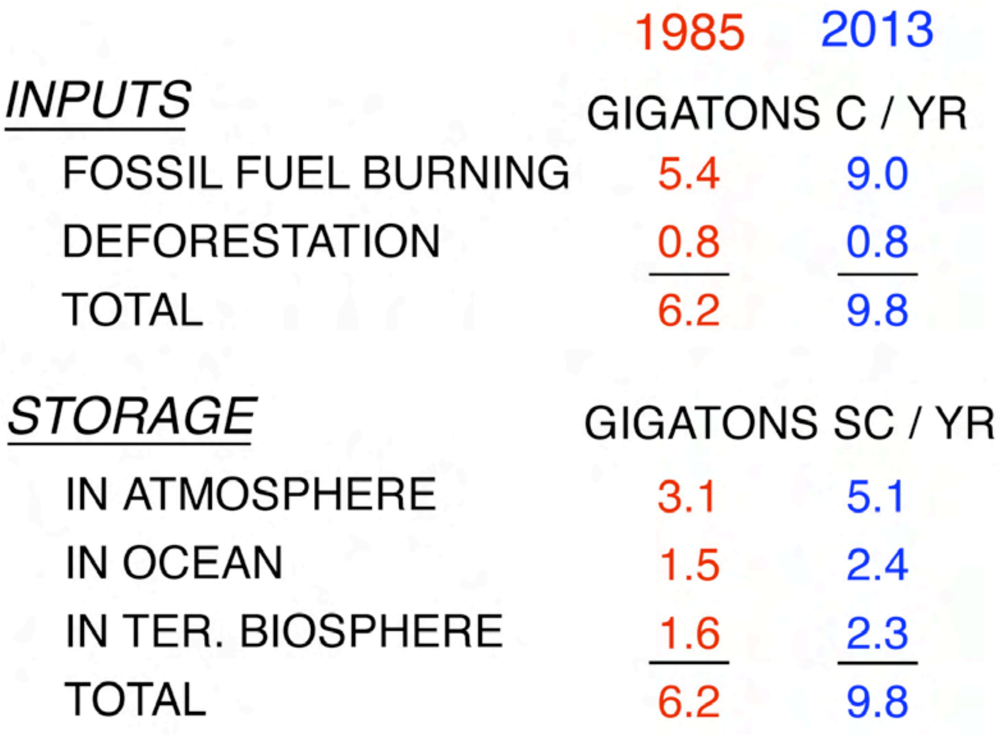


Figure 10-1. In 1958, Charles David Keeling, a scientist at Scripps Institute for Oceanography, established a station for monitoring the atmosphere's CO_2 content high on the extinct Hawaiian volcano Mauna Loa. It has documented the rise in atmospheric CO_2 content for more than half a century. It also records the magnitude of the photosynthesis-respiration seasonal cycle. CO_2 is drawn down during the warm months and rises during the cold months. The red curve represents the increase expected if 57 percent of the CO_2 produced by fossil fuel remained airborne.



	1985	2013
INPUTS	GIGATONS C / YR	
FOSSIL FUEL BURNING	5.4	9.0
DEFORESTATION	0.8	0.8
TOTAL	6.2	9.8
STORAGE	GIGATONS SC / YR	
IN ATMOSPHERE	3.1	5.1
IN OCEAN	1.5	2.4
IN TER. BIOSPHERE	1.6	2.3
TOTAL	6.2	9.8

Figure 10-2. Estimates of the amount of carbon added to the atmosphere through fossil-fuel burning and deforestation for the year's 1985 and 2013 and the fate of this carbon. Keep in mind that except for the amount stored in the atmosphere, each of these entries is subject to errors on the order 0.4 gigatons per year. Also, keep in mind that as CO_2 weighs 44/12 times more than C. Hence the burning of 9 gigatons of fossil-fuel carbon produces 33 gigatons of CO_2 gas.

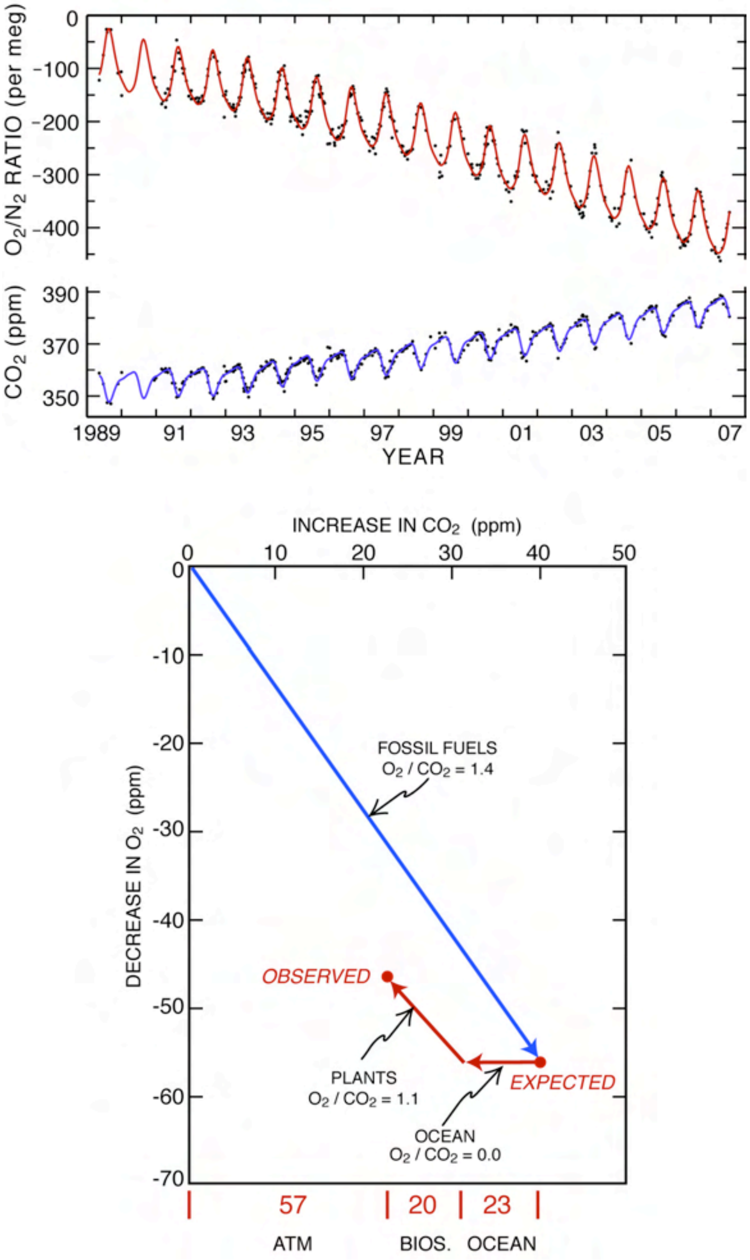
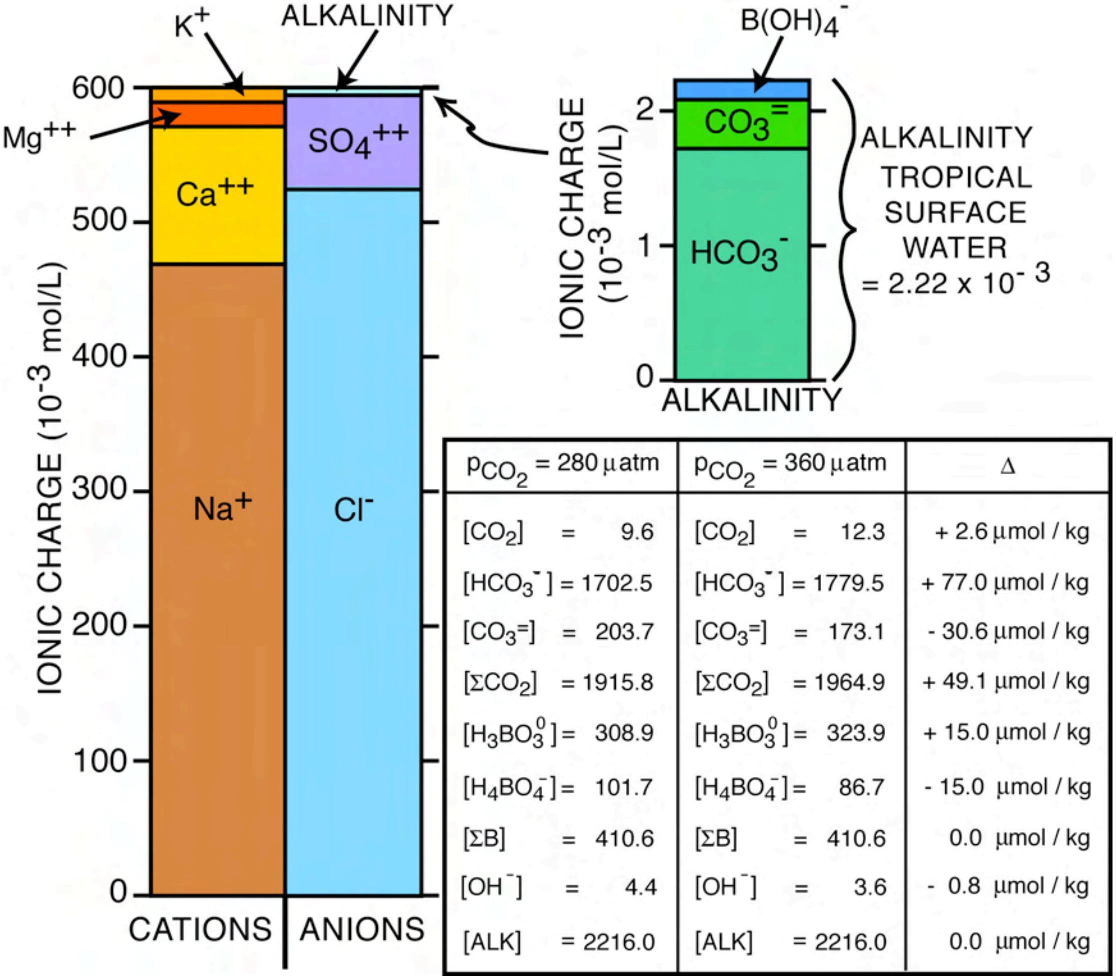


Figure 10-3. Thirty years after his father initiated atmospheric CO_2 measurements, son, Ralph Keeling, developed the means to measure the tiny decrease in atmospheric O_2. Based on samples collected on the Scripps Pier in La Jolla, California, he produced quarter-century-duration records of both CO_2 and O_2. Having both, he can place constraints on uptake by the ocean and by the terrestrial biosphere. He does this by comparing the measured extent of CO_2 increase and O_2 drawdown with that expected from the burning of fossil fuels. The important finding is that the O_2 drop was smaller than expected, requiring an increase in the amount of carbon stored in the terrestrial biosphere.



p_{CO_2} = 280 µatm	p_{CO_2} = 360 µatm	Δ
$[CO_2]$ = 9.6	$[CO_2]$ = 12.3	+ 2.6 µmol / kg
$[HCO_3^-]$ = 1702.5	$[HCO_3^-]$ = 1779.5	+ 77.0 µmol / kg
$[CO_3^=]$ = 203.7	$[CO_3^=]$ = 173.1	- 30.6 µmol / kg
$[\Sigma CO_2]$ = 1915.8	$[\Sigma CO_2]$ = 1964.9	+ 49.1 µmol / kg
$[H_3BO_3^0]$ = 308.9	$[H_3BO_3^0]$ = 323.9	+ 15.0 µmol / kg
$[H_4BO_4^-]$ = 101.7	$[H_4BO_4^-]$ = 86.7	- 15.0 µmol / kg
$[\Sigma B]$ = 410.6	$[\Sigma B]$ = 410.6	0.0 µmol / kg
$[OH^-]$ = 4.4	$[OH^-]$ = 3.6	- 0.8 µmol / kg
[ALK] = 2216.0	[ALK] = 2216.0	0.0 µmol / kg

Figure 10-4. As is the case for all matter, the salt in sea water must be electrically neutral. It turns out that the positive charge carried by potassium, magnesium, calcium and sodium is slightly larger than the negative charge carried by sulfate and chloride. This small negative charge deficit is made up by some combination of bicarbonate, carbonate and borate ions. Whereas the big six have fixed valences, the carbon and boron have adjustable charge states.

In 1850, the atmosphere's p_{CO2} CO_2 partial pressure was 280 µatm. As of 1997, it had risen to 360 µatm. As shown in the table, the resulting increase in the concentration of CO_2 gas in surface water would be only 2.6 µmol/kg. But because of the reaction between CO_2 and $CO_3^=$ ion, the total uptake of CO_2 turns out to be about 20 times greater (i.e., 49.1 µmol/kg). Two thirds of this is the result of the conversion of carbonate ion to bicarbonate ion and one third is the result of the conversion of charged borate to neutral borate. Note that no change in the alkalinity occurs. Rather it is the proportion of the three contributors which changes.

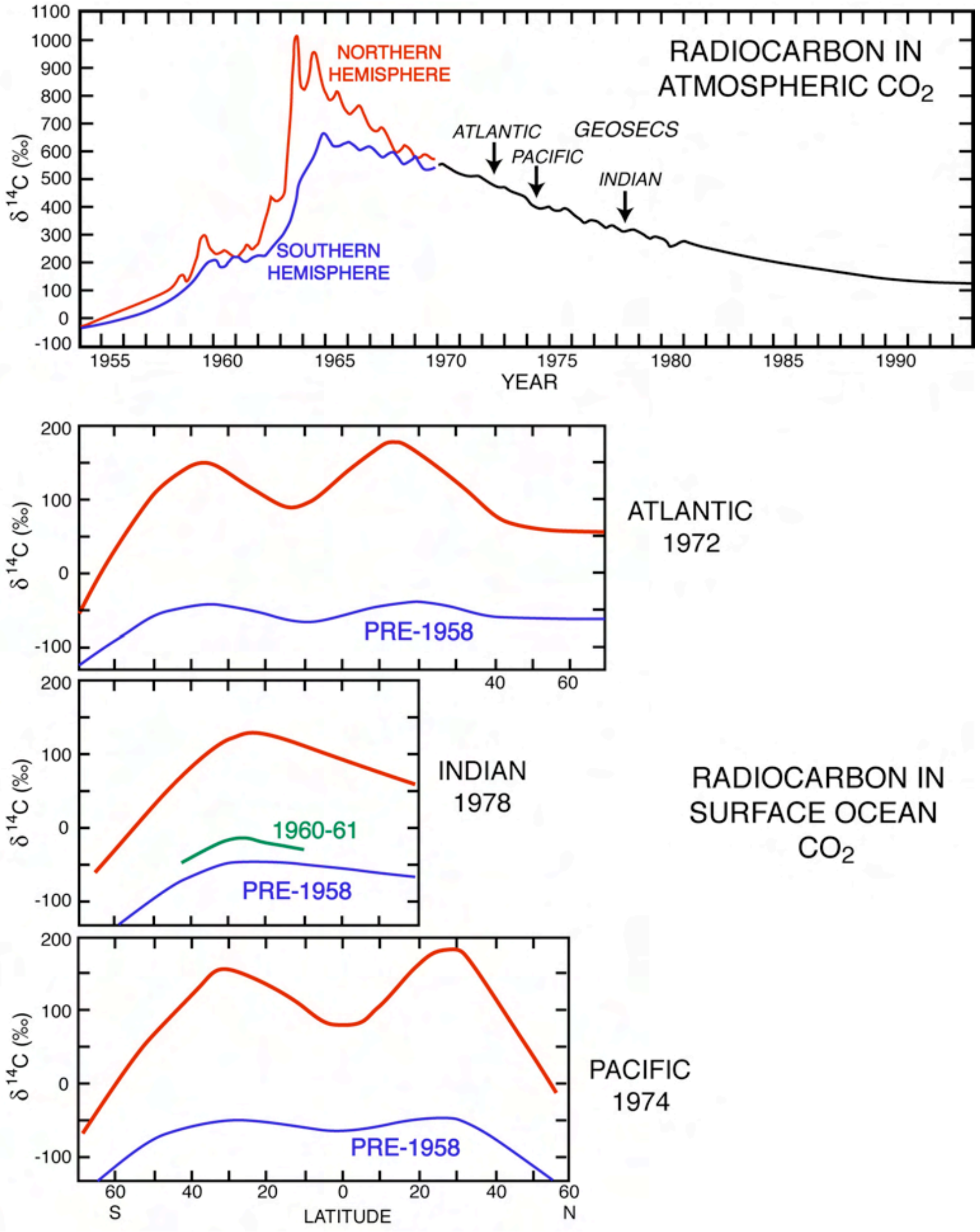
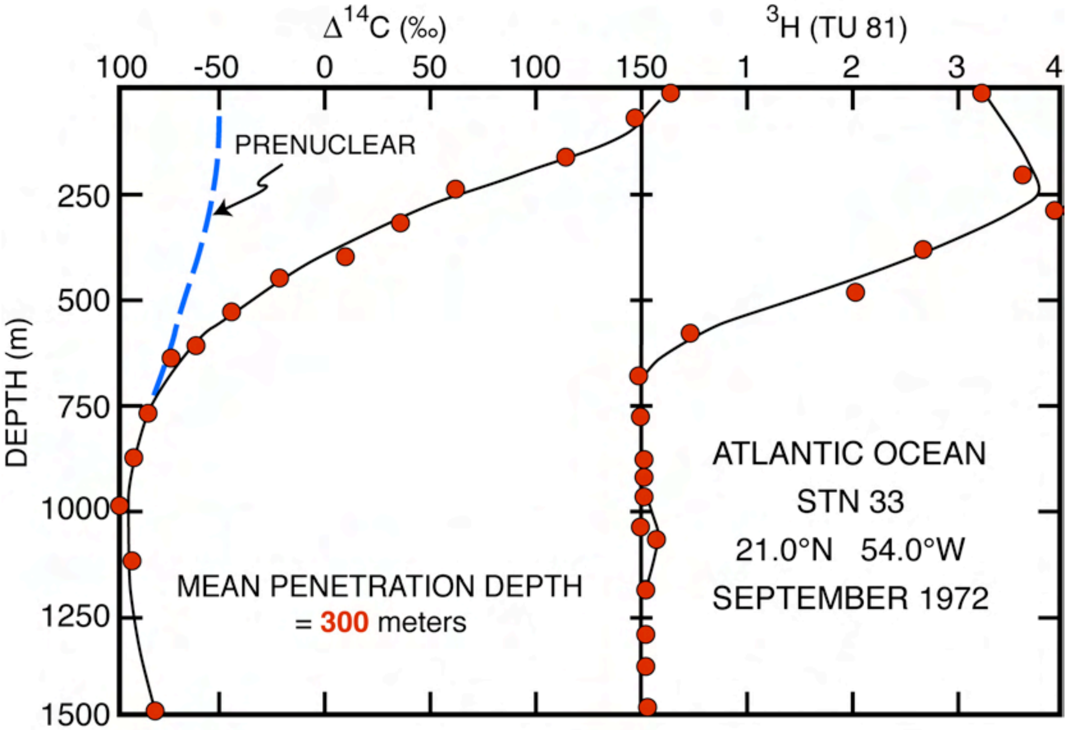


Figure 10-5. Starting in 1954, as a result of H bomb tests, the inventory of atmospheric ^{14}C began to rise. It reached a maximum nearly twice the pretesting value in 1963, six months after a ban of atmospheric testing was imposed. As the mushroom clouds generated by these tests penetrated to the stratosphere, the bomb ^{14}C was initially stored mainly in this reservoir. With time, it was transferred to the troposphere and from there to the ocean and terrestrial biosphere.

A global survey carried out during the 1970s documented the increase in radiocarbon in the upper ocean which had occurred up until that time. At the mid-point of the survey, the atmosphere excess had dropped from a 1000 per mil to about 400 per mil and the surface ocean's increase over the pre-nuclear ^{14}C to C ratio was between 100 and 200 per mil.



MEAN PENETRATION DEPTH

GEOSECS EXPEDITION		BOMB ^{3}H (meters)	BOMB ^{14}C (meters)
ATLANTIC	(1972-3)	591	414
PACIFIC	(1973-4)	336	311
INDIAN	(1977-8)	283	309
WORLD	(1972-8)	382	344

Figure 10-6. Taken together the profiles with depth of ^{14}C and ^{3}H permit the H-bomb radiocarbon contribution separated from the natural contribution. Two pieces of information allow this to be done. One is measurements of water samples collected before bomb testing and on annual growth bands in corals and shells predating H-bomb tests. The other is profiles of tritium. As the amount of natural tritium in the ocean is very small compared to that produced by man, the depth at which tritium reached zero can be assumed to be the depth at which bomb ^{14}C reached zero. The H-bomb radiocarbon profile yields an estimate of the mean penetration depth. As can be seen from the table, in the 15 or so years since this ^{14}C was created, it had penetrated the upper 10 percent of the ocean's volume. As the mean age of fossil-fuel CO_2 molecules remains about 30 years, it has penetrated about the √2 times deeper (i.e. about 15 percent of the ocean's uptake capacity has been utilized). Subsequent radiocarbon surveys have shown that its mean penetration depth has continued to increase. Now about 50 years after it was produced, it should have penetrated to about √50/12 or about two times as deep as at the time of the 1970s survey (i.e., to a depth of about 700 meters).

mean age of fossil CO_2 molecules. The longer they have been in existence, the deeper into the ocean they've gotten. The mean age of fossil fuel CO_2 molecules has remained close to 30 years. The reason is that the amount of CO_2 we produce has been rising at a rate averaging two and one half percent per year. Yes, this age will increase as we move away from the ongoing exponential rise in fossil fuel use but only very slowly. Even if we were to shut down all emissions, the age would increase by only one year per year. Further, the depth of mixing does not increase linearly with the time available. Rather it increases as the square root of time. Hence, the deepening will be correspondingly smaller.

There is however, another aspect to be considered. As fossil-fuel CO_2 heats the Earth's surface, it will strengthen the ocean's density gradients. This should slow the exchange of surface water with that in the interior and thereby decrease the rate of CO_2 uptake by the ocean.

So there are two reasons why the fraction of fossil-fuel CO_2 entering the ocean should be decreasing. First, the carbonate ion content is being depleted and second, ocean mixing may be slowing. But despite this, the atmospheric fraction has not significantly dropped. Could it be that an increase in the fractional uptake by the terrestrial biosphere has offset the decrease in the fractional uptake by the ocean?

Understanding how our multiple anthropogenic impacts have and will change the amount of carbon stored in the terrestrial biosphere remains a challenge. Two reservoirs, wood and soil organics, dominate. Above ground storage in shrubs, grasslands and agricultural plants makes only a minor contribution. Although satellite observations coupled with plot surveys have greatly strengthened our ability to assess change in the amount of wood contained in forests, progress in documenting changes in the amount of carbon stored in soils (and also in peat bogs and tundra) has been much slower. As soils store about twice the amount of carbon as trees, it is particularly important to get a better grasp on their response to anthropogenic impacts. Using H-bomb ^{14}C as a tracer, we have learned that while much of the organic matter is labile and is being replaced on a time scale of decades, there is a sizable component of inert carbon (Fig. 10-7). We know this because the bulk carbon in soils collected before nuclear testing contained about 10 percent less ^{14}C than the atmospheric carbon. In order to explain both the low pre-bomb test ^{14}C to C ratios, and also the increase following the test ban, there must be a sizable amount of soil carbon which turns over on a millennial time scale. In order to explain the ^{14}C to C transient produced by bomb-test ^{14}C, this labile fraction of soil carbon must turn over on the time scale of a few decades. Radiocarbon measurements show that the loss of carbon from agricultural plots is mainly the result of the destruction of the labile fraction (see Figure 10-7).

Yet despite the loss of terrestrial carbon as the result of forest cutting and soil manipulation, we know from global budgeting that these losses are being more than compensated by extra growth. Over the last 40 or so years terrestrial carbon storage has been steadily increasing. Three major causes have been proposed: 1) the extra CO_2 in the atmosphere is increasing the rate of photosynthesis, 2) the fixed nitrogen released from auto exhausts and from volatile farm fertilizers is finding its way to forests stimulating extra growth and hence storage, and 3) much of the lands cleared for agricultural use during what is referred to as the pioneer era have been abandoned and are being reforested. As it is difficult to quantify these contributions, reliable prediction of how the terrestrial biosphere's carbon inventory will change during the next hundred years is not possible. However as soils warm, the microbes that inhabit them will feast more rapidly. Hence, there may be a switch from increasing to decreasing soil carbon inventories. Reforestation will likely slow. But nitrogen and CO_2 fertilization will continue. Hence this is one aspect of Revelle's "experiment." It will eventually provide the answer we seek.

Although the amount of carbon stored in the terrestrial biosphere has increased during the last several decades, as indicated in simulations of ocean uptake carried out in ocean – atmosphere models require that prior to 1950, the terrestrial reservoir must have been a source rather than a sink for CO_2. Not only were fertilization by CO_2 and fixed nitrogen much smaller, but forest cutting to create farm lands was in full swing. Sometime in the middle of

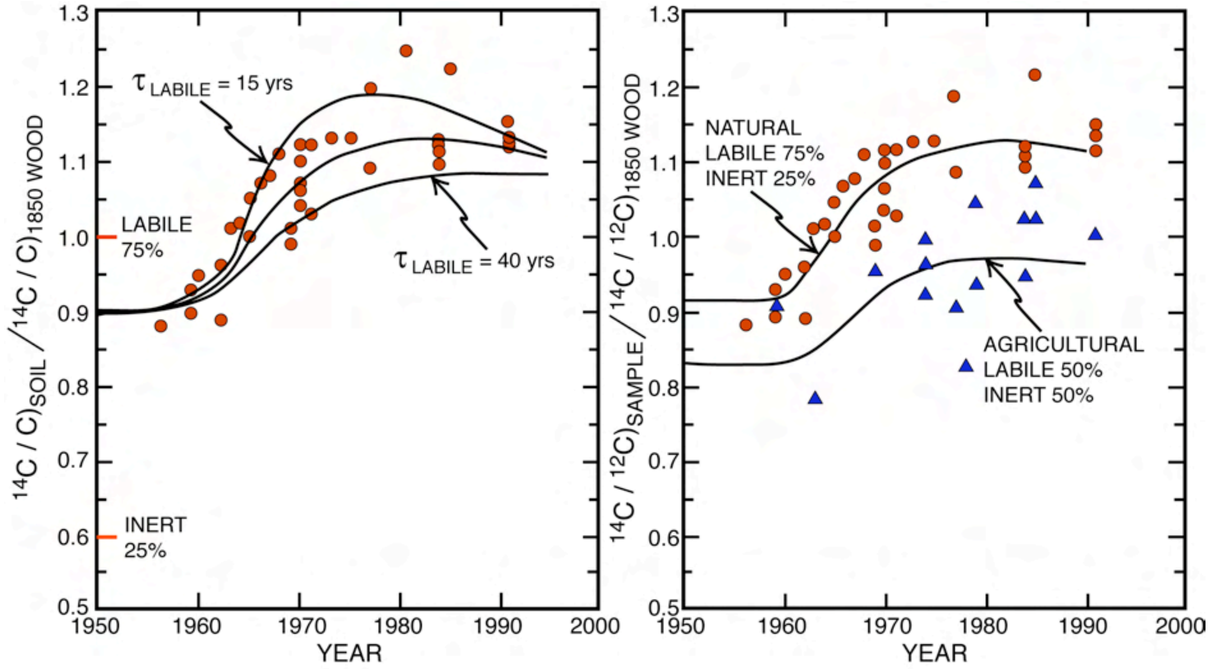


Figure 10-7. In order to match the time history of radiocarbon in soils, it is necessary to call on two pools of organic matter, one inert and the other labile. This is necessary because soils collected prior to nuclear testing had bulk ^{14}C to C ratios on the order of 10 percent lower than that in the overlying vegetation. If it is assumed that the inert carbon has an average age of 4000 years, the proportions of these two pools would be 75 percent labile and 25 percent inert. In order to explain buildup of H-test radiocarbon in the labile fraction requires that it turns over on the time scale of decades.

The difference is the time histories of ^{14}C to C ratios in agricultural soils (black triangles) with that in i.e., natural soils (red circles) is best explained by assuming that cultivation has caused a loss of labile fraction moving the points closer to that of the inert fraction. The best fit for the natural soils is that they have 75 percent labile and 25 percent inert carbon. For the agricultural soils, the split is on the average 50 percent labile and 50 percent inert carbon.

the last century, the combination of more CO_2, more fixed N_2 and the regrowth of forests in abandoned farm land led to a crossover from net loss of terrestrial carbon to a net gain of terrestrial carbon.

The concern regarding the long-term consequences of fossil-fuel burning on the Earth's biota has accelerated the study of many aspects of the carbon cycle. Satellites orbit our Earth, ships ply our seas, simulations chew up large chunks of computer time, innumerable graduate students and post docs roam the planet and man laboratories and field stations. The European Union has funded each member state to create a comprehensive carbon budget for its cities, its agricultural lands, its forests and its waterways. Those budgets are to be compared with those generated from satellite observations.

For the last 40 years, our goal has been a transition to non-fossil sources of energy. The Kyoto Accord raised our hopes in this regard. But further steps toward an international solution have yet to be taken. Predictions that the diminishment of fossil-fuel reserves would soon allow solar, wind and nuclear energy to gain an ever larger share of the energy market have proven incorrect. One reason is the exploitation of non-conventional sources of fossil fuel. Development of tar sands, fractable shales, seafloor oil reserves have fattened our diminishing reserves. Rather than leveling off and starting to decline, global consumption of fossil fuels has continued to rise at the rate of two or so percent per year. In the 1960s about 85 percent of our energy came from fossil fuels. A half century later, the ratio has not changed. We still get 85 percent of our energy from fossil fuels. In the year 1990, 20 gigatons of carbon dioxide were released to the atmosphere. In 2013, 32 gigatons were released. Currently, on the average each of the 7 billion human beings is responsible for generating 4.5 tons of CO_2 each year.

Making matters worse, a host of deniers are dedicated to stop any action directed toward stemming the rise of CO_2. In the U.S., backed by large injections of corporate money, these deniers have carried out with religious fervor an extremely effective campaign. They have succeeded in cowing both Congress and the President.

So what can we do? Of course the first order of business is to do everything possible to reach utopia. By ‘utopia’, I mean a world fueled by renewables. But, the experience of the last 40 years tells us that in absence of some dramatic sociological and technological breakthroughs achieving this goal will require many decades. In order to halt the rise in CO_2, emissions will have to be cut by at least tenfold. As it will take hundreds of years for the ocean to suck up its full share of fossil-fuel CO_2, in order to speed up the removal we will likely have to institute negative emissions.

By negative emissions I mean removal of CO_2 from the atmosphere. It is inevitable that at some point this will be done. In an ideal world, we would begin tomorrow. But, there is currently no indication that the world is comfortable with even seriously considering such a course of action, let alone implementing it. Hence, it will likely not happen until the atmosphere’s CO_2 content reaches a level where its consequences become prohibitively expensive. Only then will we bite the bullet and launch the mammoth effort that will be required to draw CO_2 back down to an acceptable level.

This being the case, we should have a backup plan. One leg of this plan would be to develop the capability to capture and bury CO_2. The capture could be from the exhaust of electrical power plants (stack capture) or from the atmosphere (air capture) (Fig. 10-8), or more likely both. Burial could either be in the pores of sandstones or the cracks in basalt. Enough is known to state that this could very likely be financed by a 20 percent add-on to the cost of fossil-fuel energy. But far more must be learned before such an effort could be launched on a large scale. And the scale would be large indeed. If, as the proponents of air capture propose, it were to be done with modular units capable of capturing one ton of CO_2 per day, 100 million such units would be required to remove CO_2 at the rate we are currently releasing it. Hundreds of million more would be required to draw CO_2 back down.

The CO_2 pulled out of stacks and out of the air will have to be buried. Feasible storehouses include sandstones and basalts (Fig. 10-9). Although storage in the lakes beneath

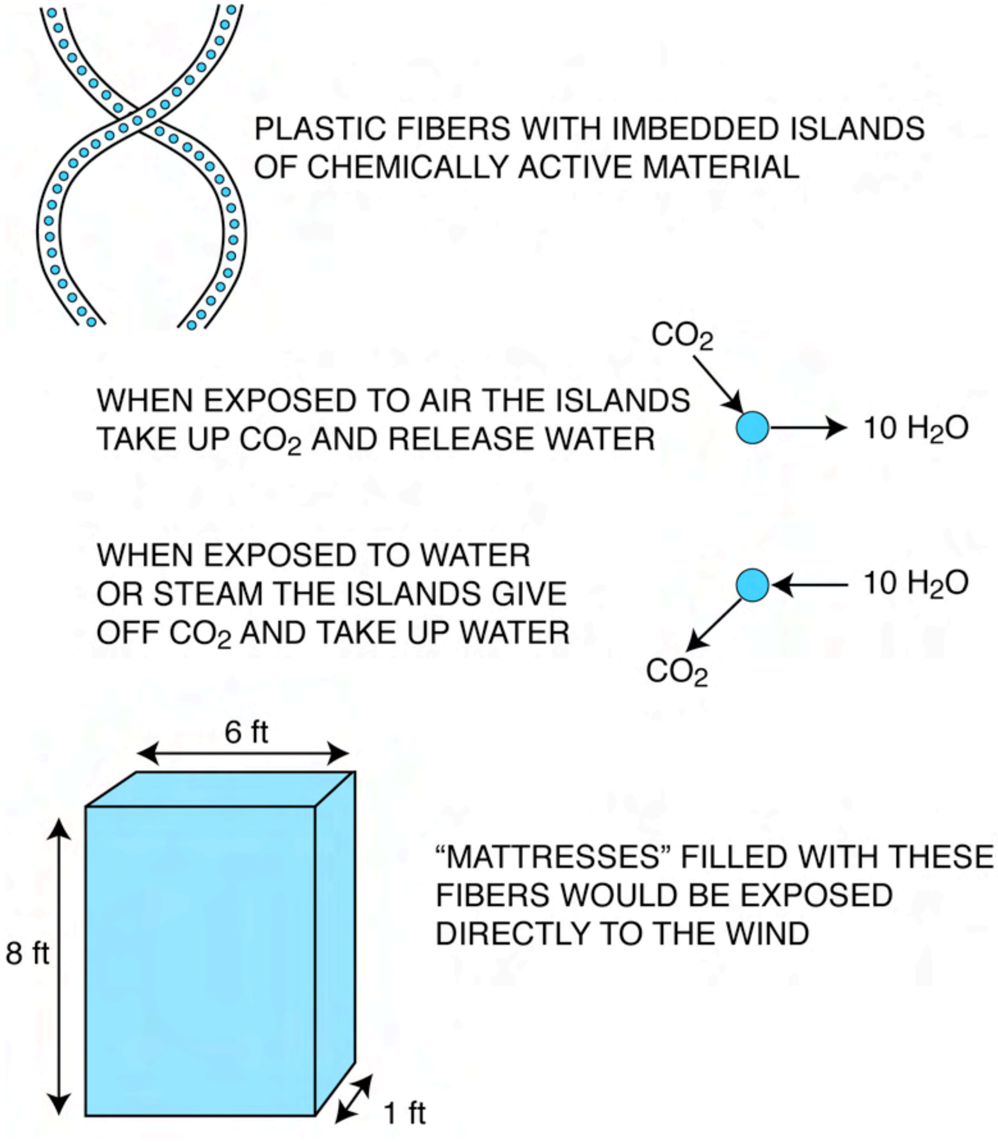


Figure 10-8. The currently most promising absorbent for pulling CO_2 directly out of the atmosphere is a plastic imbedded with chemically active islands which exchange H_2O for CO_2. These fibers would be packed into mattresses which would be exposed to the wind. The plastic has three important advantages. 1) It is solid; 2) it can recycle CO_2 and H_2O without any loss of capacity, and 3) the energy required to free the captured CO_2 is five times less than would be the case for sodium hydroxide.

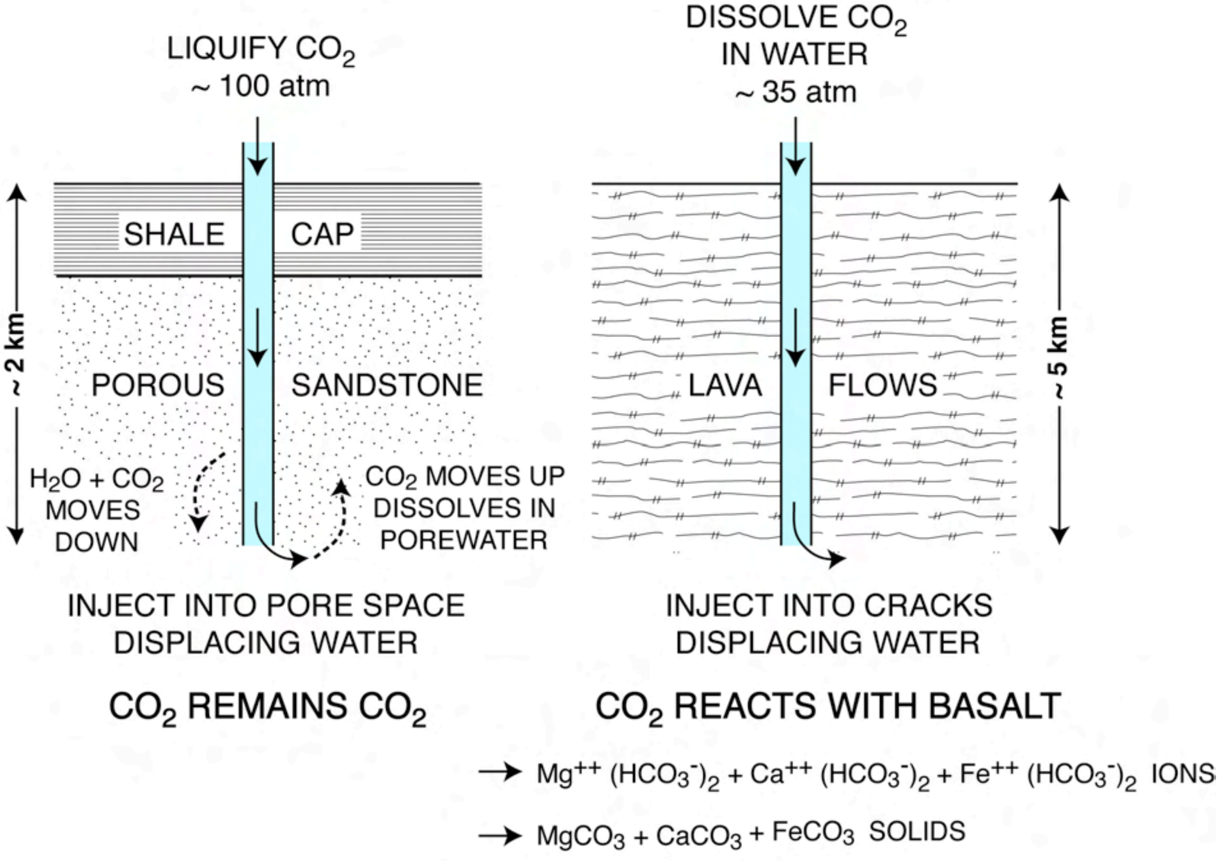


Figure 10-9. CO_2 captured from power plant exhausts or directly from the atmosphere must be stored. Two options are presently on the table. One involves the injection of CO_2 into the water- filled pores in sandstones and the other involves dissolving the CO_2 in water and injecting it into the cracks in basalt. As the quartz grains in sandstone contain no soluble cations, the CO_2 remains CO_2. As liquid CO_2, it is less dense than water. It would initially slowly rise. But when it dissolves in the surrounding pore water, the water would become ever more dense until it would begin to slowly sink. An impermeable shale cap ensures that the CO_2 will not find its way back to the surface. Storage in basalt has the advantage that the CO_2 reacts with the pyroxene and plagioclase releasing Mg, Ca and Fe ions which react with the CO_2 converting it to bicarbonate (and carbonate) ions. When the product of Ca^{++}, Mg^{++} or Fe^{++} and $CO_3^=$ reaches saturation, the minerals $CaCO_3$, $MgCO_3$ and $FeCO_3$ will form. The reason that the CO_2 is pre-dissolved in water is to ensure that it doesn't leak to the surface. As the partial pressure of the CO_2 in the injected water will not exceed that of the confining pressure at the injection depth, there will be no tendency for the CO_2 to escape. The required water could be pumped up from the basalt (i.e., recycled).

the Antarctic ice caps and in the deep sea are scientifically attractive options, because of their possible environmental consequences, they are unlikely to be utilized. Storage in the pores of sandstones is already being done. For two decades, Norway's Statoil has been removing CO_2 from the methane recovered from beneath the North Sea. The CO_2 is separated, liquefied and pumped back down a kilometer or so into the sandstone where it displaces the water filling the pores. Seismic imaging shows that the buoyant liquid CO_2 is slowly rising. However, before it reaches the overlying impermeable shale barrier, it will dissolve in the surrounding water. As the water laden with extra CO_2 is more dense than water without extra CO_2, it will then slowly move back down.

Burial in basalt has a major advantage over that in sandstone. While sandstone has no cations capable of immobilizing CO_2 by conversion to HCO_3^-, basalt has abundant Fe^{++}, Ca^{++} and Mg^{++} ions. An experiment conducted in Iceland involved injecting CO_2 dissolved at high pressure in water into basalt. Within days, this CO_2-acidified water was neutralized by reaction with cations dissolved from the rock. Within months much of the CO_2 had been mineralized to form Fe, Ca, and Mg carbonates.

One of the advantages of air capture is that it can be carried out directly above the storage site. This obviates the use of high pressure pipelines to carry the liquid CO_2 from urban power plants to distant storage sites. Further, as CO_2 capture from the atmosphere is most efficient when carried out under low humidity conditions, capture and storage could be carried out in dry wastelands well away from population centers. Further, the required energy could be derived from local sunshine and wind (Fig. 10-10).

As reduction of the atmosphere's CO_2 content by capture will take a long time and cost a lot of money, there will be those who will opt for an alternate route referred to as geoengineering. It involves compensating for the greenhouse effect of the extra CO_2 by increasing the Earth's reflectivity. Model simulations tell us that doubling CO_2 is equivalent to dialing up the Sun's energy output by about two percent. Hence, if we could somehow reflect away two percent of the sunlight reaching the Earth, we could at least on the average

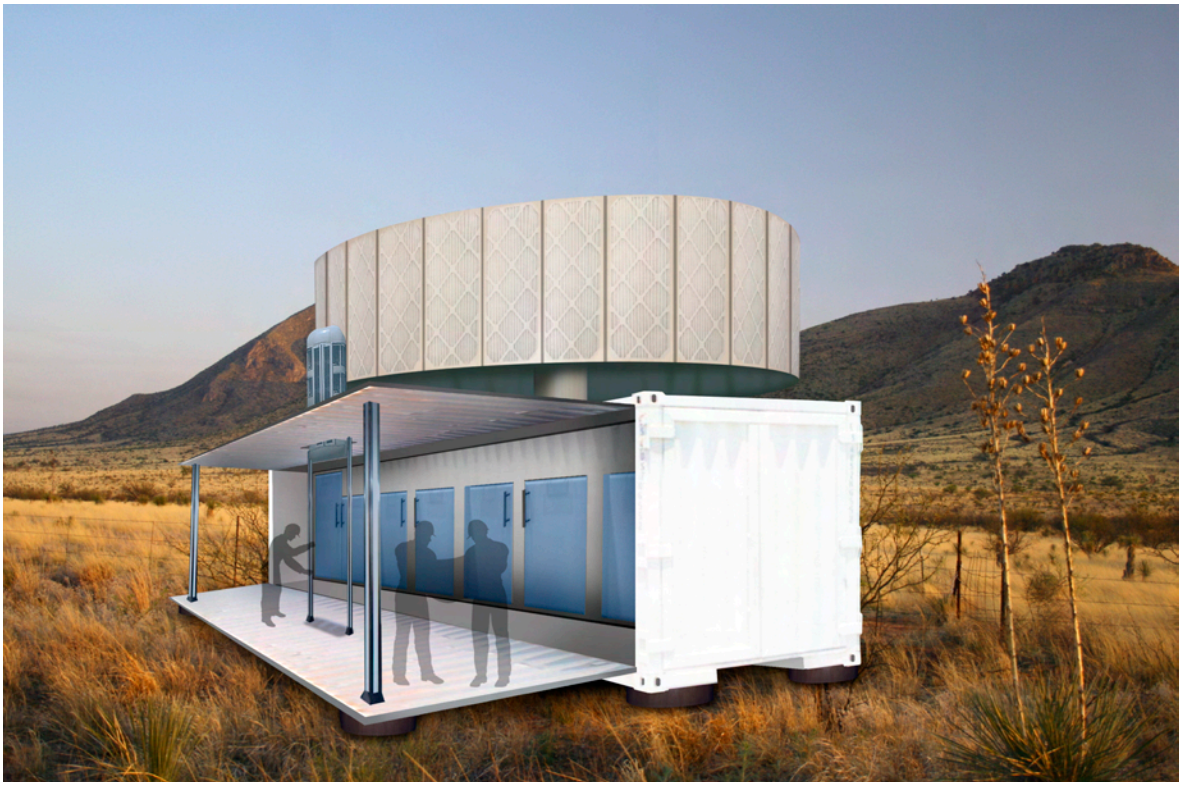


Figure 10-10. Air capture would likely be done using modular units capable of capturing about one ton of CO_2 per day. Fiber-packed "mattresses" would be deployed above chambers in which the CO_2 would then be recovered from the fibers and freed of air. The recovered CO_2 would be stored in either sandstone or basalt.

In order to collect the 30 billion tons of CO_2 currently being produced would require the deployment of 100 million such units. As the fibers are more efficient in dry air, these units would be placed in remote dry lands located above suitable storage strata.

undo the CO_2 warming.

A half century ago Mikhail Budyko, a Russian scientist, proposed that this might be accomplished by adding SO_2 to the stratosphere. Once there, this gas would be promptly oxidized to tiny H_2SO_4 aerosols which would reflect away part of the sunlight which encountered them. Two major volcanic eruptions have provided tests of Budyko's idea. Mexican volcano, El Chichon, erupted in 1982, and Philippine volcano, Pinatubo, erupted in 1991. Both injected large amounts of SO_2 into the stratosphere. Within weeks this SO_2 had been converted to H_2SO_4 aerosols. These aerosols remained in the stratosphere for a year or two before being mixed down onto the troposphere where they purged by incorporation into raindrops. After both eruptions, there was a short-term drop in Earth temperature.

By putting together information gained from observing the aftermath of these eruptions with that from laboratory studies, flesh has been added to Budyko's suggestion. The aerosols were shown to average 0.3 microns in diameter. Aerosols of this size back-scatter about 10 percent of the rays which strike them. Based on this, in order to compensate for a doubling of CO_2, 20 percent of the sunlight reaching the Earth would have to pass through these manmade aerosols. Two percent would then be reflected back to space. To maintain this inventory would require the yearly addition of about 30 million tons of SO_2 to the stratosphere.

Those favoring the geoengineering approach point to its favorable cost compared to that for CO_2 capture and storage. A year's dose of SO_2 would cost about 100 billion dollars. At 100 dollars a ton, in order to remove the 30 billion tons of CO_2 we currently add each year would cost about 3000 billion dollars, i.e., about 30 times more. If the cost of SO_2 addition were to be shared equally by everyone on the planet, the per capita tax would be about 13 dollars a year. By contrast, the per capita tax for stabilization of the atmosphere's CO_2 content would be more like 400 dollars a year. To draw CO_2 back down would cost correspondingly more. Proponents of geoengineering would also point out that cooling by albedo modification could be accomplished in a period of a few years while it would likely take decades to accomplish the same cooling by CO_2 removal.

Those opposing geoengineering would counter 'yes, it's cheap and it's fast, but it's a Band-Aid, not a cure.' These aerosols could bring the Earth's average temperature down to any desired level, but it is unlikely that they would return climate to what we now have. For example, the distribution of rainfall would likely differ from that prior to the fossil fuel era. In a world where fresh water had become a precious commodity, this could lead to conflict. Further, the acidification of seawater created by the continuing CO_2 buildup would add to the stress on coral and other $CaCO_3$ precipitating organisms. Finally, we would have to continue to inject SO_2, for were we to stop, the planet would warm back up.

Which path will we take? Unfortunately both will likely be necessary. Even when the realization that it must be done finally sets in, we are unlikely to be able to carry out air capture fast enough. Let's say we wanted to cool the Earth in a decade. To do so would require the removal of on the order of 1200 billion tons of CO_2 or 120 billion tons per year. This would require 400 million one-ton-a-day air capture modules. The cost would be 20 trillion dollars a year or 1600 dollars per year per Earth inhabitant. Looked at this way, the price of SO_2 remediation would be 100 times cheaper than rapid CO_2 removal. Hence in a world strapped for money, the temptation to use SO_2 as a stopgap will be very strong.

So we are poised to take over the control of the atmosphere's CO_2 content. Given enough time, we certainly have the where-with-all to maintain it at any desired level. But as 180 or so nations will have a say as to what level this should be, making a choice will prove difficult. But if there is an upside to Roger Revelle's experiment, it is that during the course of this century we will get a glimmer of what the world's climate would be like at wide range of atmospheric CO2 contents.

Environmentalists cringe at the thought of either of these solutions. They would say we could avoid both CO2 capture and SO2 cooling if we could get our energy from the Sun with some help from wind and nuclear. Of course, they are correct. The problem is that we aren't making the transition. Fifty years ago, about 85 percent of our energy came from fossil fuels. Today about 85 percent of our energy comes from fossil fuels. When at last we do get around to switching to renewables, the cost will be comparable to that of air capture, for almost all of our energy infrastructure will have to be replaced.

References for Chapter 10

Broecker W., (2013), Does air capture constitute a viable backstop against a bad CO_2 trip? *Elem. Sci. Anth. 1*: 000009 doi: 10.12952/journal.elementa.000009.

Broecker, W. S., and T.-H. Peng (1998), *Greenhouse Puzzles*, Eldigio Press, NY; Revised Edition.

Goldberg, D. S., K. S. Lackner, P. Han, A. L. Slagle, and T. Wang (2013), Co-location of air capture, sub-seafloor CO_2 sequestration, and energy production on the Kerguelen Plateau, *Environmental Science and Technology, 47*, 7521-7529.

Hansen, J., M. Sato, P. Kharecha, D. Beerling, R. Berner, V. Masson-Delmotte, M. Pagani, M. Raymo, D. L. Royer, and J. C. Zachos, (2008), Target atmospheric CO_2: Where should humanity aim? *Open Atmos. Sci. J.*, *2*, 217-231.

Keeling, R. F., S. C Piper., and M., Heimann (1996), Global and hemispheric CO_2 sinks deduced from changes in atmospheric O_2 concentration, *.Nature*, *381*, 218-221,

Lackner, K. S., S. Brennan, J. M. Matter, A.-H. A. Park, A. Wright, and B. van der Zwaan (2012), The urgency of the development of CO_2 capture from ambient air, *PNAS*, *109*, 13156-13162.

Langdon, C., T. Takahashi, C. Sweeney, D. Chipman, J. Goddard, F. Marubini, H. Aceves, H. Barnett, and M. J. Atkinson, (2000), Effect of calcium carbonate saturation state on the calcification rate of an experimental coral reef, *Global Biogeochem. Cycles*, *14*, (2), 639- 654.

Oelkers, E. H., S. R. Gislason, and J. M. Matter, (2008), Mineral carbonation of CO_2, *Elements*, *5*, 333-337.

Acknowledgements

Over the decades, conversations with Michael Bender have buffeted my thinking. Throughout his career, he has had an eye out for ways to gain insight into past ocean chemistry. Of late, he has hit pay dirt, by analyzing a suite of aragonitic corals spanning the last 120 million years. Once published, these results will surely have a large impact on our thinking about the evolution of the composition of sea salt.

Many other names of people who have inspired my thinking regarding polar chemistry come to mind. In particular, Dan Schrag, Jeff Severinghaus, Flip Froelich, Karlis Muehlenbachs, Danny Sigman, John Eiler, John Higgins, Bärbel Hönisch, Harry Elderfield, Jim Wright, Dennis Kent, Anne Gothmann and the late John Edmond. A very special thanks goes to Scott McLennan who provided a detailed set of suggestions as to how this manuscript could be improved.

This book would never have come into being without the help provided by two very special people, Patricia Catanzaro and Joan Totton. Patty created the 80 or so illustrations and Joan the 80 or so text pages.

Finally, my wife, Elizabeth Clark, kept me going in a hundred ways. Without her, I'm sure that I would have thrown in the towel or gone off the tracks years ago.